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AESF/EPA (American Electroplaters and Surface Finishers/Environmental Protection Agency) Conference on Pollution Control for the Metal Finishing Industry (8th) Held at San Diego, California, February 9-11, 1987

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Society, Orlando, FL

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The 8th Annual AESF/EPA Conference and Exhibit on Pollution Control for the Metal Finishing Industry was held in San Diego, California, February 9, 10 and 11, 1987. The program was organized by Dr. Rebecca Spearot, member of the American Electroplaters and Surface Finishers Environmental Committee and Roger Wilmoth of the United States Environmental Protection Agency, Manufacturing and Service Industries Branch.

The primary objective of the 8th Conference was to continue the dialogue established by the first AESF/EPA Conference in 1978 between key members of the Agency and the metal finishing industry. The program featured key EPA representatives who explained and discussed regulatory guidelines in detail; in addition, leading industrial experts discussed industry's efforts to dffectively address the ramifications of the EPA regulations.

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8TH AESF/EPA CONFERENCE ON POLLUTION CONTROL FOR THE METAL FINISHING INDUSTRY

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DISCLAIMER

The following papers have been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication:

Hazardous Waste Research Pertaining to Metal Finishing
Treatment of Aqueous Metal Bearing Hazardous Wastes
Optimizing Transfer Efficiency of Spray Painting Operations
Pilot Scale Results of Metal Value Recovery From Mixed Metal Hydroxide Sludges

The following papers describe work that has not been funded by the U. S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred:

Plating Waste Sludge Metal Recovery
Why Not Simplify Wastewater Compliance?
Liability for Managing Hazardous Wastes: Past, Present and Future
How Clean Is Clean? (What Constitutes the Clean Closure of a Hazardous Waste Land Management Facility?)
Installation of a New Nickel/Chromium Plating Facility
Pollution Control Using Room Temperature Evaporators
Howard Plating Cleans Up Their Act With Magnesium Hydroxide
Metal Finishing Wastewater Treatment Upgrade with an Insoluble Sulfide Precipitation Process
The Performance of Analytical Test Kits of Metal Finishing Wastewater Samples
Application of Statistical Process Control to Wastewater Pretreatment
Wastewater Reduction in Metal Fabrications Operations
Wastewater Treatment: Optimizing an Existing System
Electrolytic Recovery: Theory, Application, Advantages
Waste Treatment and Recycling of Mixed Wastewater From a Metal Finishing Company
Environmental Auditing: Management's Key to Effective Environmental Compliance
Successful in House Recovery of Solvent
Calpurnia and the Strip Barn
Emissions from Chrome Plating Scrubbers as a Function of Scrubber Liquor Concentration

The panel discussions of February 9-11 were taped and are available from American Electroplaters and Surface Finishers Society, 12644 Research Parkway, Orlando, FL 32826, telephone (305) 281-6441.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report contains 22 separate papers that have a direct impact on the metal finishing industry. The papers were prepared by industry research and regulatory personnel. The information contained in this report should prove beneficial to those individuals directly interested in this industry segment. For further information, contact the Industrial Wastes and Toxics Technology Division.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

The 8th Annual AESF/EPA Conference and Exhibit on Pollution Control for the Metal Finishing Industry was held in San Diego, California, February 9, 10 and 11, 1987. The program was organized by Dr. Rebecca Spearot, member of the American Electroplaters and Surface Finishers Environmental Committee and Roger Wilmoth of the United States Environmental Protection Agency, Manufacturing and Service Industries Branch.

The primary objective of the 8th Conference was to continue the dialogue established by the first AESF/EPA Conference in 1978 between key members of the Agency and the metal finishing industry. The program featured key EPA representatives who explained and discussed regulatory guidelines in detail. In addition, leading industrial experts discussed industry's efforts to effectively address the ramifications of the EPA regulations.

The 8th Conference was attended by over 425 individuals interested in environmental problems. The proceedings are published in order that the important material presented at this Conference can be of benefit to as many people as possible. Inasmuch as the Monday afternoon regulatory papers were not available for publication, the Society arranged to tape the sessions and the subsequent panel discussions on Monday. These cassettes may be ordered from the AESF Book Department, in care of AESF Headquarters, 12644 Research Parkway, Orlando, FL 32826.

The EPA and the AESF are pleased to continue this mutual endeavor which has improved communications and which should force the continued research and sound technical solutions to the environmental problems of the surface finishers. The 9th Conference is planned to be held late January, 1988, in Orlando, Florida.

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NOTE: Complete Papers for Session I are not available. However, the Session has been taped in its entirety and a cassette may be ordered from the AESF Book Department, 12644 Research Parkway, Orlando, FL 32826.

HAZARDOUS WASTE RESEARCH PERTAINING TO METAL FINISHING

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The Environmental Protection Agency (EPA) has conducted research to evaluate or develop metal waste control techniques for a number of years. This paper presents a brief description of the more important projects that have been conducted since 1978. These projects include efforts of the programs that are conducted not only by the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory, but also those conducted by the Manufacturing and Service Industries Branch of the Water Engineering Research Laboratory. Within EPA's research program, these two Laboratories manage all of the engineering research activities of the Agency that deal with hazardous metallic wastes. During the past year, work has centered on the performance assessment of commercial facilities treating these wastes and evaluation and development of a waste reduction audit procedure.

Our preference for the management of any waste stream is represented by the following hierarchy:

- Waste elimination,
- Recycle,
- Reuse,
- Burn as fuel,
- Incineration,
- Chemical/biological detoxification,
- Volume reduction, and
- Solidify and dispose.

The performance evaluations of existing treatment technology/waste stream combinations were done to determine the best demonstrated available technology (BDAT) for that waste stream. Previously, a report[1] provided an evaluation of the sources and extent of cyanide and metal-bearing hazardous wastes and an analyses of current management practices for treating or disposing of these wastes. It includes an examination of the costs of current practices and the residuals and the emissions from treatment systems. Treatment schemes were identified which will chemically or physically treat these wastes to make them acceptable for land disposal. This information was used to develop the plan for our performance evaluation program. There are three parts to our research efforts: (1) field performance evaluations, (2) pilot tests at our Test and Evaluation Facility in Cincinnati, and (3) examination of ways to reduce wastes. Our efforts are designed to determine acceptable ways to handle or treat wastes so that they may be land disposed.

WASTE MANAGEMENT APPROACH

The Agency's approach to managing hazardous wastes will be to require that the waste stream, after treatment, passes three tests before it may be land disposed. The first test is the "paint filter" test. This is a simple test to ensure that the waste does not contain free moisture before it is land disposed.

The Agency is considering two further tests. The first concerns the land diposal restriction, or BDAT number. For each hazardous component that may be present in a particular listed waste, EPA will establish maximum concentrations that are permissible in order for that waste to be disposed of to the land in a secure hazardous waste disposal facility. This maximum concentration will be the lowest concentration that can be achieved through treatment with the BDAT.

The other test is the proposed toxicity characteristics leaching procedure (TCLP). This is a test to determine if a waste exhibits sufficiently low toxicity that it can be disposed of to the land in a non-secure land disposal facility. This TCLP contains a health-based limit for a number of organic compounds and metals. If the leachate found through the TCLP contains concentrations of the TCLP listed compounds in excess of the limits established for the TCLP, the waste must be treated until the waste passes the TCLP.

FIELD PERFORMANCE EVALUATIONS

Field performance evaluations have been conducted for the sites listed in Table 1. The cooperation of industry with the EPA in the conduct of this performance evaluation program has been quite good. This cooperative spirit between the industry and the Government is essential in order to arrive at common-sense decisions regarding the management of these wastes. The most important findings from these tests show that there are current practices that produce a residual that contains such sufficiently high levels of organic materials that it is unable to pass the TCLP test as it is currently specified. There does not appear to be a problem in passing the EP Toxicity Test. BDAT for these wastes has not yet been codified. The Hazardous and Solid Waste Amendments of 1984 establish the statutory limits for land disposal restrictions for metal-bearing and cyanide materials that will go into effect July 7, 1987.

Table 1

TEST SUMMARIES

LANDFILL BAN PERFORMANCE EVALUATION PROGRAM

SITES TESTED JUNE 1985 TO APRIL 1986

Waste Codes	Waste Composition	Waste Source	Treatment Technology
D002 Spent Nitric Acids and Metals	38% Nitric Acid (E) 5-10% Copper (E) <0.1% Organics (E) 50+% Water (E)	Electronics (Printed Circuit Board Manufacturing)	Neut./Lime Addition/ Precipitation/ Centrifugation/ Reclaimed Metal
D002, D004 Mixed Aqueous Metal-Laden	2% Arsenic (E) 25% Nitric Acid (E) 3% HF (E) 70% Water (E)	Aerospace, Auto Manufacturing	Chemical Coag./ Precipitation/ Sedimentation/ Evaporation/ Carbon Adsorption
D002, D007, F006 Waste Paint Sludge, Waste Plating Sludge, Cleaning Solution	Paint Sludge (E) Zinc Phos. Sludge (E) Biopond Sludge (E) Metal Sludge (E)	Auto Manufacturing Petroleum Air Force Base	Solidification w/Fly Ash
D002 Mixed Aqueous Metal-Laden	<5% Metals (E) <0.1% Organics (E) 95% Water (E) Trace CN (E)	Electrical Components, Applicance Manufacturing	Lime Addition/ Precipitation/ Filtration/ Carbon Adsorption
F007 Cyanide Rinse	<0.5% Metals (E) 500 ppm CN (E) 99% Water (E)	Plating	Cyanide Dest. (alkaline chlorination followed by aqueous waste treatment)

PLANNED PILOT-SCALE TESTS

At our Test and Evaluation Facility, we will evaluate the effectiveness of heavy metal reduction; waste concentration; removal of organic interferences, such as chelating agents, strongly complexing anions or organics which hinder heavy metal precipitation; and stabilization/solidification processes. For each system, we hope to establish the overall treatability efficiency, characterize the residuals resulting from the use of that system, and establish ways to remove interferences. The facility is designed to enable our in-house researchers to respond quickly to specific questions on waste stream treatment/technology combinations.

WASTE MINIMIZATION EFFORTS

During the past year, we have completed case studies of waste minimization programs at three plants that produce metal-laden wastes. Two of the studies were at printed circuit board manufacturers. These studies concentrated on rinse waters that follow electroplating and etching processes. The third plant manufactured mobile communication equipment components. The focus at this plant was on the second stage of a system designed to recover TCE from the first-stage stillbottoms. Reports on each of these studies are currently being prepared.

A waste reduction audit procedure has been developed and tested. It provides a methodology for identification, assessment and screening options for waste minimization. The specific objectives of our projects are:

- To generate a comprehensive list of waste minimization measures or options applicable to a specific industrial process; and
- To rank all identified waste reduction options and use these rankings to allow management to focus on options deserving further in-depth consideration.

We believe this audit procedure will help find ways to meet the RCRA requirement to certify that the volume or quantity and toxicity of hazardous wastes have been reduced to the degree economically practicable.

Several barriers that inhibit implementing waste management actions can be easily overcome by a cooperative attitude by plant management. These barriers are such things as:

- Lack of awareness;
- A "hands off the process" attitude caused by fear of upsetting a product's quality;

- Organizational inertia--"if it isn't broken, don't fix it" attitude;

- Internal politics of the organization (for example, an innovator may feel inhibited by a fear of the lack of management's support); and

- An "it can't be done" attitude; people may reject an innovative approach merely because it is outside their range of experience.

A paper by Carl Fromm and Michael Callahan discusses the audit procedure and presents a case study of its use.[2]

PAST RESEARCH PROJECTS[3]

The Environmental Protection Agency has sponsored research into metal removal and/or recovery from wastewaters and sludges for over ten years. Early efforts concentrated on precipitating metals to protect waters but the wisdom of also reclaiming metal was soon recognized as a means of reducing water pollution while conserving metal resources. Work done for EPA at Battelle Columbus in 1975 included a survey of plating facilities and the volume and types of metals discarded in sludges. As understanding of the problem began to develop, a series of investigations was funded, each adding to the overall bank of information. These projects are listed in reverse chronology below.

Metal Value Recovery from Metal Hydroxide Sludges[4]

The latest EPA projects were undertaken at the Montana College of Mineral Science and Technology (Montana Tech) and tied together much of the previous work. The first phase of the investigation was a carefully executed series of laboratory experiments to establish the processes needed to leach hydroxide sludges (the most plentiful type produced by electroplating shops) with sulfuric acid, and the various recovery methods required for copper, zinc, chromium, and nickel. Flowsheets were developed and the unit operations required to make a complete recovery process were developed.

In phase two, a pilot assembly capable of processing 75-100 lbs. of sludge per day was built and operated at a large electroplating facility. While not entirely troublefree, the operation was smooth enough to allow confirmation of the possible commercial viability of the process, and development of a computerized mass balance.

The steps of the process were as follows.

- The sludge is leached with sulfuric acid.

- Iron, which is frequently present in EP sludges, was removed by precipitating as a potassium jarosite $[KFe_3(SO_4)_2(OH)_6]$. This must be done first, as iron interferes in many of the subsequent recovery steps. This step is in need of improvement, because in the process of precipitating the jarosite some anions such as chromate are removed, along with some heavy metal cations. Even though the volume of the jarosite sludge is much less than that of the starting material, the waste would be classed as hazardous, requiring special precautions and extra costs when landfilling. Because of these faults, it is proposed that a new program be instituted to attempt to remove iron without the inclusion of large amounts of other heavy metals.

- Conventional techniques were used to extract copper from the acid solution using an oxime in petroleum solvent. The copper was then stripped from the organic phase with stronger acid and electrowon or crystallized as sulfate.

- Zinc and cadmium were extracted with diethyl hexyl phosphoric acid (D_2EHPA), leaving chromium and nickel behind. Again, a sulfuric acid strip was used for zinc removal from the organic phase. Small amounts of residual iron are removed in early stages of extraction; ten extraction stages are required to remove iron-free zinc.

- Chromium was oxidized to Cr^{+6} with chlorine, then selectively precipitated as lead chromate which can be sold as a pigment or regenerated to chromic acid with sulfuric acid. The lead sulfate precipitate formed when chromic acid is regenerated may itself be recycled to precipitate more lead chromate. In some instances SO_2/O_2 oxidation of the chromium may be more desirable.

- Nickel is precipitated as sulfide, the only heavy metal in the process which is not directly recyclable back to a plating operation. However, several alternative techniques are presented to yield a nickel ammine, or nickel sulfate may be solvent extracted with a mixture of chelating agents.

Recognizing that some improvements could be made in the various separation steps, first order cost estimates indicate that a 50-ton per day recovery plant could not only reduce landfill volume considerably, with consequent less chance of pollution, but in addition could yield a profit as shown in Table 2.

Metal Recovery from Electrochemical Machining and Electrodischarge Machining (ECM/EDM) Wastes[5]

These relatively new machining processes produce heavy metal wastes; ECM yields hydroxide sludges heavily contaminated with sodium chloride, and EDM

Table 2

PROCESS COST: FIRST ORDER ESTIMATE

UNIT OPERATION	COST ($)*			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electro-winning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100
Profit (Gross)			1,071,900	

*Assuming a $1.00 per gallon credit for sludge from producers.

finely divided particles of the alloy being machined. Both ECM and EDM are primarily used on hard alloys, often high in nickel, chromium, cobalt, molybdenum, etc. This project involved a survey of ECM/EDM shops, the volumes of sludge produced, metal content, and disposal practices and costs. Several recovery routes were studied, including the procedures outlined above.

Cadmium Recovery from Electroplating Wastes[6]

This project was primarily concerned with methods and costs for recovering cadmium from plating shops which are able to segregate Cd from other sludges, or perhaps those whose only business is cadmium plating. The authors give very little thought to the fact that many platers use cadmium at least occasionally, and do not segregate their sludges. The recovery technique (melt and/or distill cadmium electromotively displaced with zinc metal) is most effective on low chromium and nickel sludges. While chromium is not displaced by zinc, nickel would have to be removed by distilling the zinc.

Coupled Transport Systems for Control of Heavy Metal Pollutants[7]

Coupled transport membranes are made by immersing a microporous membrane into a liquid complexing agent such as those used for liquid/liquid extraction of metals from solution. The liquid (often called a liquid ion exchanger) then acts as a transfer agent to move metal ions through the capillaries, using the driving force of the pH gradient across a membrane separating an acidic from a basic solution. Data are presented which suggest that a membrane unit having 450 to 500 square feet of surface could separate chromium from the rinse water of a medium sized plating line. The separation unit would cost about $5,000, compared to over $50,000 for an evaporative-ion exchange system.

Evaporative Recovery of Chromium Plating Rinse Waters[8]

A demonstration of this process was given by Advance Plating Company, Cleveland, Ohio on the first of four counterflow rinse tanks. After first passing through a cation exchanger to remove metallic impurities, water from the first rinse tank is drawn into a vacuum evaporator, whose condensate is returned to the third rinse tank. Concentrated acid produced in the evaporator bottoms is returned to the plating bath. The value of recovered chrome has enabled the operator to pay off the equipment in two years or less, in addition, the chromic acid in dragout water is reduced by 99.98%.

Removal of Toxic Metals from Metal Finishing Wastewater by Solvent Extraction[9]

This short investigation of solvent extraction was primarily limited to one extraction agent, Alamine 336 (General Mills). By increasing acidity stepwise with HCl, selective removal of chromium, cadmium, and zinc from wastewaters was demonstrated. Copper and nickel could not be extracted with this reagent; several other high molecular weight amines were tried without success.

Reverse Osmosis Field Test: Treatment of Watts Nickel Rinse Waters[10]

Rinse waters from a Watts type (primarily nickel sulfate) nickel plating operation were passed through a polyamide membrane, effectively separating a concentrated nickel salt solution and recycling the rinse water. Results were very encouraging, indicating that the capital cost of the R.O. unit could be recovered in about a year, based on the reduction in water usage plus metal values returned to the plating bath. This process could be more accurately described as recycling or conservation since there is no chemical change of metals recycled to the bath.

Treatment of Metal Finishing Wastes by Sulfide Precipitation[11,12,13,14]

Although the process of sulfide precipitation has been known for many years, its use as a means of pollution control appears to be of fairly recent origin, and, is mentioned here primarily to illustrate an effective method of metal removal. A major disadvantage of sulfide precipitation is the lack of selectivity; it is apparently impossible to precipitate a single metal without major contamination by other metal sulfides. Use of a polymeric flocculant (preferably anionic) increased the settling rate, and adding a chelating agent such as EDTA (ethylenediamine tetraacetic) acid at the proper pH greatly aided selectivity.

Heavy metal sulfides, even if effectively separated, are extremely difficult to reduce to their corresponding metals by hydrometallurgical methods, and are generally recovered by smelting. The large volumes of raw material required to support such smelters makes plating waste metal recovery by this method impractical.

A Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges[15]

A survey of plating opertions involving over 600 questionnaires (150 replies) revealed the extent of sludges generated by the industry, and even developed a "typical" analysis of metal content; the copper, nickel, and chromium contents were very similar to those found in subsequent studies. Some preliminary laboratory leaching and extraction studies led to the conclusion that metal recovery could be economically feasible only if the process could be carried out on a large, and preferably continuous scale. Based on then current (1971) metal prices, it was concluded that chromium and zinc recovery were uneconomic; the writers apparently did not foresee the ban on landfilling of heavy metal wastes now being implemented.[12] The only laboratory work done by these investigators was leaching experiments with ammonium carbonate and sulfuric acid which indicated that acid leaches were adequate for most hydroxide sludges while ammonium carbonate would only dissolve copper and nickel. A literature study of several potential recovery methods for copper and nickel was made, but no work was done to verify their efficacy; again, chromium recovery was not considered.

NOTICE

This report has been reviewed by the Hazardous Waste Engineering Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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PILOT SCALE RESULTS OF METAL VALUE RECOVERY
FROM MIXED METAL HYDROXIDE SLUDGES

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INTRODUCTION

Metal finishing hydroxide sludge materials are produced as a result of pollution control technology to remove heavy metal contaminants from electroplating spent electrolytes and rinse waters. Presently, most of these solids are disposed of in hazardous waste sites. The Environmental Protection Agency has supported several projects directed toward treatment of metal finishing hydroxide sludges for metal value recovery (1,2,3).

It has been demonstrated that conventional hydrometallurgical unit operations can be applied to mixed metal hydroxide sludge materials (1). Effective and selective separations of metal values from complex mixed metal solutions have been accomplished, e.g., separation of Fe, Cu, Zn, Cr, Ni. However, two unit operations are high cost and high energy processes, i.e., removal of iron and oxidation and subsequent recovery of chromium.

The present study was initiated to investigate an alternative and potentially more cost-effective way for removing iron and recovering chromium from mixed metal solutions, i.e., bench scale test work by Dahnke (4) has shown that trivalent cations can very effectively be stripped from solutions in preference to divalent cations under conditions of low pH and at room temperature by phosphate precipitation. The successful application of simple precipitation of iron and chromium from mixed metal solutions could mean elimination of the two high cost, high energy unit operations:

- iron removal by jarosite precipitation (the unit operation used in the previous(1) study to remove iron) requires near boiling temperatures and long residence times (four-six hours) whereas phosphate precipitation can be accomplished at room temperature in thirty to sixty minutes.

- chromium recovery by oxidation to chromate with subsequent precipitation as a solid chromate and conversion to chromic acid requires that a difficult and slow oxidation be accomplished by use of chlorine gas or by an electrochemical cell, whereas phosphate precipitation strips chromium (+3) from solution and aqueous oxidation is unnecessary.

The substitution of relatively simple precipitation processes for the above more complex processes should significantly increase the cost-effectiveness of the overall metal value recovery sequence. The present study was, therefore, initiated to demonstrate that the bench scale separation results could be achieved on a larger more significant scale. This presentation is, then, a progress report on our efforts to demonstrate selective and effective metal value recovery from several actual electroplating sludge materials. The project is not yet complete and will continue through July, 1987 (5).

Features of the Phosphate Process

Previous bench scale studies have resulted in the development of potential flowsheets to accomplish the separation of metal values from releached hydroxide sludge materials (3,5,6,7). The treatment process is based on the selective precipitation of phosphate compounds.

Important features of the phosphate process include (7):

- Selectivity in acid solution for removal of trivalent cations from divalent and monovalent cations. Therefore, Fe(+3) or Al(+3) or Cr(+3) can be precipitated selectively from Zn(+2), Ni(+2), Cd(+2), Na(+1), etc., bearing solutions. Also trivalent cations can be, in some cases, selectively separated from other trivalent cations.

- Solid/Liquid Separation is excellent because the precipitated phase consists of agglomerated spherites. The filterability feature is very important, i.e., the phosphate products filter easily and can be compacted to a high solids content.

- Conversion of the phosphate precipitate to a hydroxide product (and subsequently to a disposable or marketable product) regenerates the phosphorus reagent for reuse; thereby improving the process economics.

Selectivity of the Phosphate Process

Stability diagrams provide useful data for designing metal separation flowsheets. Illustrative examples are presented in Figures 1 and 2 for trivalent cations and in Figures 3-5 for divalent cations (7). Superimposition of these diagrams allows the user to predict the possibility of potential selective separations of metals from an aqueous solution; e.g., iron from nickel (see notes on Figure 6); iron from zinc (see notes on Figure 7). From such diagrams it is apparent that iron(+3) should be selectively precipitated from nickel or zinc in acid solutions.

In general, trivalent cation phosphates can be stripped selectively from solutions containing divalent or monovalent cations under acid conditions. Similar general statements can be made concerning the precipitation of trivalent hydroxides from divalent hydroxides. However, hydroxide solids are difficult to separate from solution and are highly contaminated by other cations by surface adsorption. Phosphate precipitates are readily filterable and do not absorb solution cations to the extent that hydroxide precipitates do.

RESULTS AND DISCUSSION

Bench Scale Test Work

Bench scale test work conducted at Montana Tech on relatively pure synthetic solutions and on actual sludge multicomponent leach solutions are reported elsewhere (3,4,6-10). The results of these studies have shown that:

- Iron phosphate (precipitated particle morphology is shown in Figure 8).
  - precipitation is rapid (essentially complete in 0.5-1 hr), Figure 9 (4,7).
  - precipitation to less than 20 mg/liter can be accomplished from an acid solution at a pH ∿ 2.5, 25°C, without nickel or chromium coprecipitating, Figure 10 (5).
  - precipitation is temperature independent up to at least 56°C, Figure 11 (7,9).
  - filterability of the precipitated ferric phosphate is excellent, Table 1 (7,9).
  - ferric phosphate can be effectively converted to ferric hydroxide with the regeneration of the phosphate reagent, Figure 12 (10). The resulting ferric hydroxide is non-toxic, i.e., it passes the EP Toxicity test.
  - conditions necessary to precipitate ferric phosphate are essentially the same for a sulfate or chloride aqueous solution, Figure 13 (4,8,9).
  - precipitation is selective over divalent cations such as zinc, nickel, and cadmium, Figure 14 (4).
- Chromium Phosphate (precipitated particle morphology is shown in Figure 15).
  - chromium phosphate precipitation is very temperature dependent. Room temperature precipitation does

not occur until the solution pH is raised to 3.5 (in a one hour time interval), Figure 16 (7).

- precipitation is rapid (0.5-1 hr), effective (<10 mg/liter) and selective over divalent cations such as zinc, cadmium, nickel at a pH of 3.5 at 57°C, Figure 14 (5); at 61°C and 83°C, Figure 17 (5).

- filterability of the high temperature chromium phosphate is excellent.

- conditions necessary to precipitate chromium phosphate are essentially the same for a sulfate or chloride aqueous solution.

A great deal of emphasis has been given to separation of the trivalent cations of iron and chromium from mixed metal solutions because their removal is necessary before the other valuable metals can be recovered without iron and/or chromium contamination:

- the removal of iron from mixed metal solutions is a high cost unit operation (1) if done by high temperature jarosite precipitation, solvent extraction, or hydroxide precipitation.

- the removal of chromium (+3) from mixed metal solution is a high cost unit operation (1) if done by oxidation to chromate and recovery by precipitation or ion exchange.

Recovery of the divalent metals such as nickel, zinc and cadmium can be accomplished by conventional hydrometallurgical unit operations once the trivalent metals have been removed (1), e.g., solvent extraction of zinc and precipitation of nickel hydroxide or nickel carbonate.

Flowsheet Applications

The objective of the large scale test work was to demonstrate on a significant quantity of material that selective separations could be acccomplished. The test system consisted of leach and precipitation vessels (including heaters and agitators) large enough to accommodate on a batch basis the treatment of up to two hundred liters of slurry; a filter press; and auxiliary pH control and monitoring instrumentation.

A number of different flowsheets can be formulated to treat a given sludge material. However, a common feature of most of the visualized flowsheets is that iron must be removed first, then chromium before any of the divalent metals. The divalent metals can also be removed by phosphate precipitation but other hydrometallurgical unit operations are available and may be used depending on the desired final product.

Four sludge materials are being considered in the present study and a variety of flowsheets are being used to demonstrate the versatility of the process. Two of the flowsheets will be discussed in this presentation, i.e., flowsheets to treat an iron-chromium-zinc electroplating sludge, and an iron-chromium-nickel electromachining material.

Fe-Cr-Zn

The flowsheet used to treat an iron-chromium-zinc sludge material is presented in Figure 18. This material was obtained from an operation engaged in zinc phosphatizing of steel parts and chromium plating final products. Therefore, the sludge is composed primarily of iron-chromium-zinc-phosphate. The sludge is high zinc and chromium with appreciable iron and calcium.

The treatment sequence consisted of acid leaching sufficient sludge to produce 200 liters of starting mixed metal solution containing approximately forty grams per liter dissolved metals; solid/liquid separating the leach residue; oxidizing the ferrous fraction to ferric by air and precipitating ferric phosphate; solid/liquid separating the ferric phosphate; precipitating chromium phosphate at an elevated temperature; solid/liquid separating the chromium phosphate; precipitating zinc phosphate; solid/liquid separating the zinc phosphate.

The starting sludge and product compositions are presented in Table 2. The unit operations and experimental conditions are depicted in Figure 18. EP toxicity test results on the leach residue are presented in Table 3. Elemental distribution among the various products are presented in Table 4. The following general conclusions are noted for this test work:

- Sulfuric acid leaching was very effective in redissolving the metal values; e.g., extraction efficiences are presented in Table 5. The leach unit operation produced 200 liters of a solution containing 3.1 gpl Fe, 2.7 gpl Cr, 3.2 gpl Zn.
- The weight of residue resulting from the leach unit operation was about forty percent of the weight of the starting solid. This particular sludge producer used lime as the neutralizing agent rather than caustic. Therefore, the leach residue was predominantly calcium sulfate (the leach residue weight resulting from most sludge leach solutions neutralized with caustic is about fifteen percent of the starting sludge).
- The residue passed the EP toxicity test (11) and can, therefore, be disposed of in a non-hazardous waste site.
- Ferric phosphate was effectively removed from solution, only 133 mg/liter remained after precipitation. The chromium content of the ferric phosphate solid was only 2.41%.
- The ferric phosphate passed the EP toxicity test. Therefore, if a market does not exist it can be converted to hydroxide (with

the regeneration of phosphate reagent) and can be disposed of in a non-hazardous waste site.

- Chromium phosphate was effectively removed from solution, only 90 mg/liter remained after precipitation. The iron content of the product was only 0.84%; the zinc content only 0.37%.

- Zinc phosphate was effectively removed from solution, e.g., <1 mg/liter remained after precipitation. The zinc phosphate contained only 0.17% iron and 0.57% chromium. This material should be marketable as a phosphatizing material.

- The final solution contained only 0.64 mg/liter Cr, <0.1 mg/liter Fe, <0.1 mg/liter Zn. A part of this volume can be recycled as make up water for the leach operation, i.e., about twenty percent can be recycled. The remainder can be treated by evaporation to produce a sodium sulfate crystalline product.

Fe-Cr(+6)-Ni

The flowsheet used to treat an iron-chromium(+6)-nickel sludge is presented in Figure 19. This material was a sludge produced by an electrochemical machining facility. It contained the chromium in a mixed valence state, e.g., about 80% chromium(+6), 20% chromium(+3). Also the sludge solids were about 30% sodium chloride.

The treatment sequence consisted of acid leaching; ferric phosphate precipitation; solid/liquid separation; chromium(+6) reduction to chromium(+3) and elevated temperature precipitation of chromium phosphate; solid/liquid separation; nickel phosphate precipitation; solid/liquid separation.

The starting sludge and solids composition are presented in Table 2.EP toxicity test results for ferric phosphate are presented in Table 3. Elemental distribution among the various products are presented in Table 4. The following general conclusions are noted for this test work:

- Sulfuric acid leaching was very effective in redissolving the metal hydroxides of iron, chromium, and nickel. Some of the nickel present in the starting sludge was present as metallic particles (along with niobium) that do not readily redissolve. If the leach residue can be separated, it would be a high value product because of its nickel and niobium content, e.g., the residue (which makes up about 9% of the starting solids) contains 19.3% Ni, 43.1% Nb, and 7.2% Ti.

  The high nickel-niobium fraction was not separated in the present test work because the available filter press cloths were not appropriate to make the separation.

The leach unit operation produced 191 liters of solution containing 3.21 gpl Fe, 2.29 gpl Cr, and 7.76 gpl Ni.

- Ferric phosphate was precipitated from the solution containing the metallic particle residue. The iron content remaining in solution was only 35 mg/liter. The ferric phosphate solid contained only 0.87% Cr but was, of course, high in nickel, niobium, and titanium, because of the presence of the unfiltered metallic fraction, e.g., 2.79% Ni, 3.86% Nb, and 2.39% Ti.

  The EP test results (Table 3) showed only nickel above one hundred times the drinking water standard. However, if the metallic fraction had been separated the ferric phosphate solid would have passed the EP test.

- Chromium phosphate was effectively removed from solution, only 28 mg/liter of chromium remained after precipitation. The iron content of the product was only 0.18%, the nickel content was 2.99%. Chromium phosphate would have to be converted to a more marketable product such as chromic oxide by a simple pyrometallurgical fusion process. The nickel would be separated from the chromium during the fusion conversion process.

- Nickel phosphate was removed to a level of 62 mg/liter nickel. Further lowering can be achieved by precipitating at a higher pH.

  The solid nickel phosphate product contained only 0.06% Fe but contained 1.54% Co.

- The final solution contained 0.28 mg/liter Fe, 0.21 mg/liter Cr, and 62 mg/liter Ni. A part of this volume can be recycled as make-up water for the leach operation. The remainder can be treated by evaporation to produce a sodium sulfate crystalline product and a solution more concentrated in nickel and chromium for recycle to the leach unit operation.

Summary

The flowsheet results presented in the previous section illustates that metal values can be recovered from electroplating and electromachining sludge waste materials. The major advantages of using phosphate precipitation over other possible separation unit operations are the simplicity of the precipitation and the ease of solid/liquid separation.

A large number of alternative flowsheets are possible. The selection of the most appropriate treatment sequence will depend on the products desired and product marketability. The treatment of mixed metal hydroxide sludge materials cannot be economically carried out by individual metal platers, i.e., relatively large quantities of sludge must be treated to justify the cost of the required multistep separations. A first order economic analysis is presently being performed for a flowsheet to treat fifty tons of sludge per day of a copper-iron-chromium-zinc-nickel composite material. The unit operations involved in the analysis consists of:

- copper solvent extraction to produce crystalline copper sulfate.
- iron removal by phosphate precipitation; conversion of the phosphate to ferric hydroxide for landfill disposal. Phosphate reagent will be regenerated for recycle to the iron precipitation reactors.
- chromium removal by phosphate precipitation; conversion of the chromium phosphate to chromic oxide by sodium carbonate fusion.
- zinc solvent extraction to produce crystalline zinc sulfate.
- nickel removal by carbonate precipitation.
- recycle of a portion of the final solution as make-up water and treatment of the remainder of the solution by evaporation and recycle to the leach operation.

The results of the cost estimates will be reported in the final report to EPA in July.

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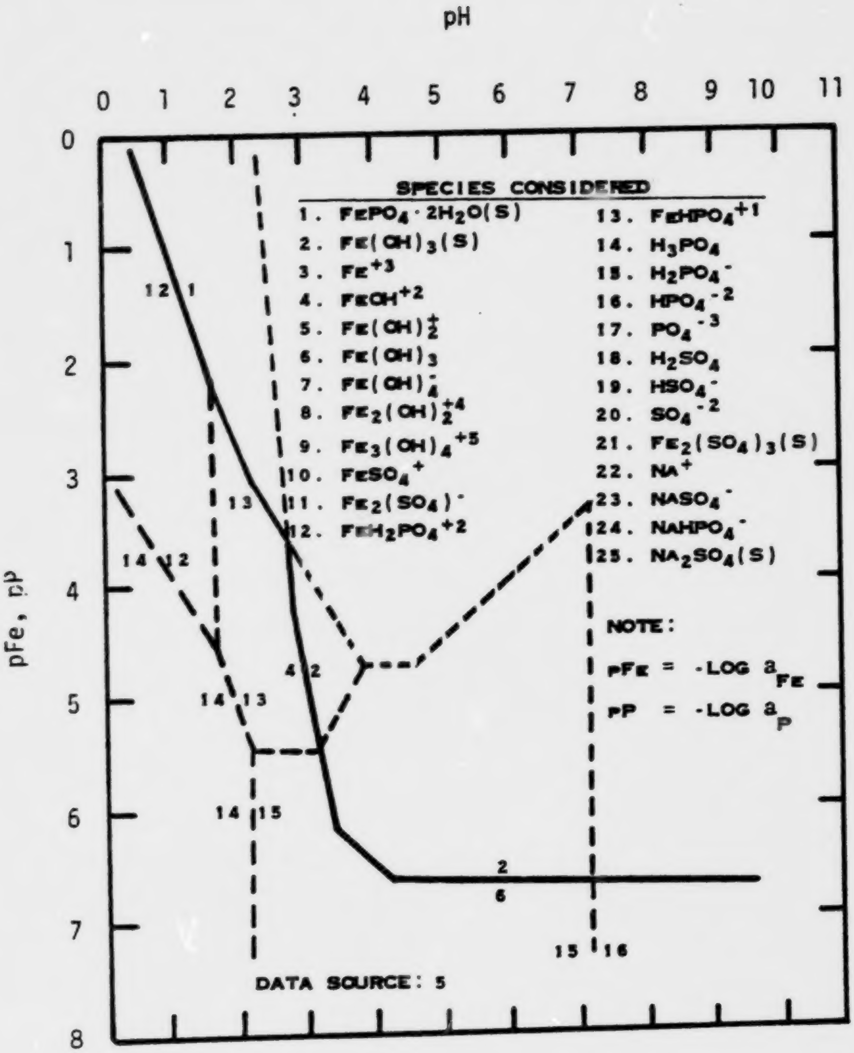


FIGURE 1. FERRIC PHOSPHATE STABILITY DIAGRAM FOR THE FERRIC-PHOSPHATE-SULFATE-WATER SYSTEM(7).

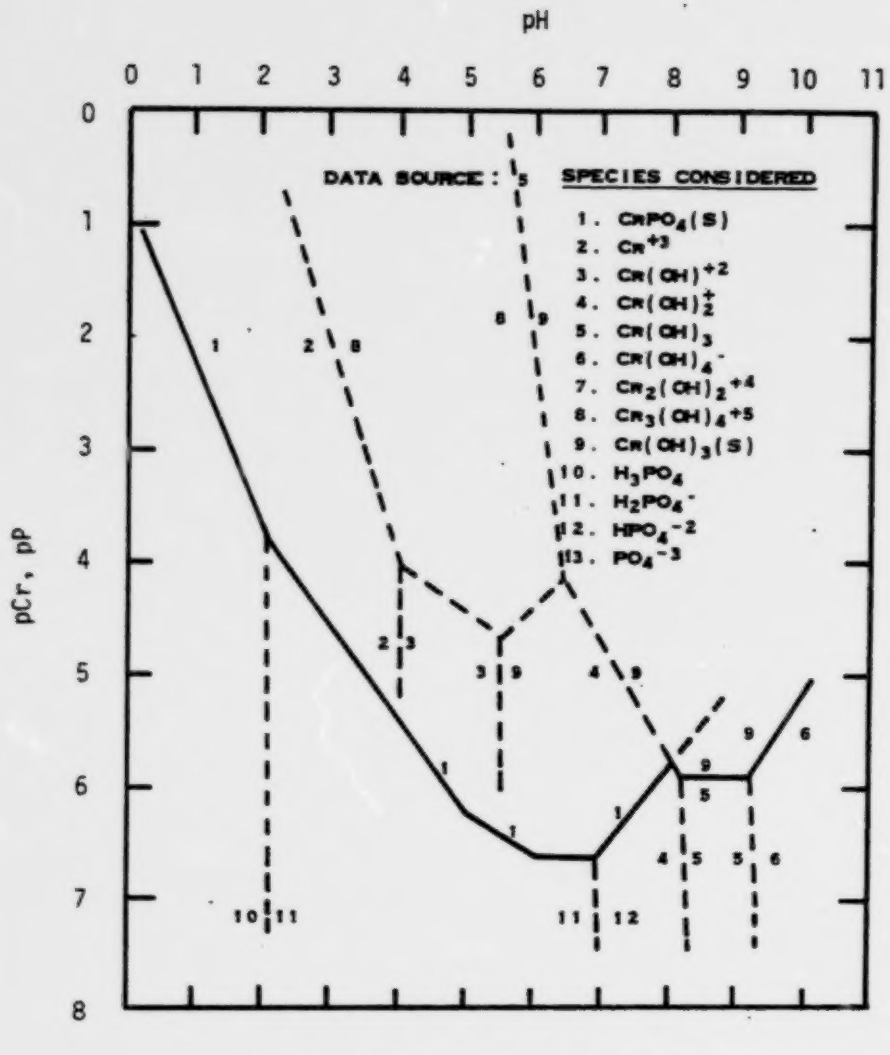


FIGURE 2. CHROMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CHROMIUM-PHOSPHATE-WATER SYSTEM(7).

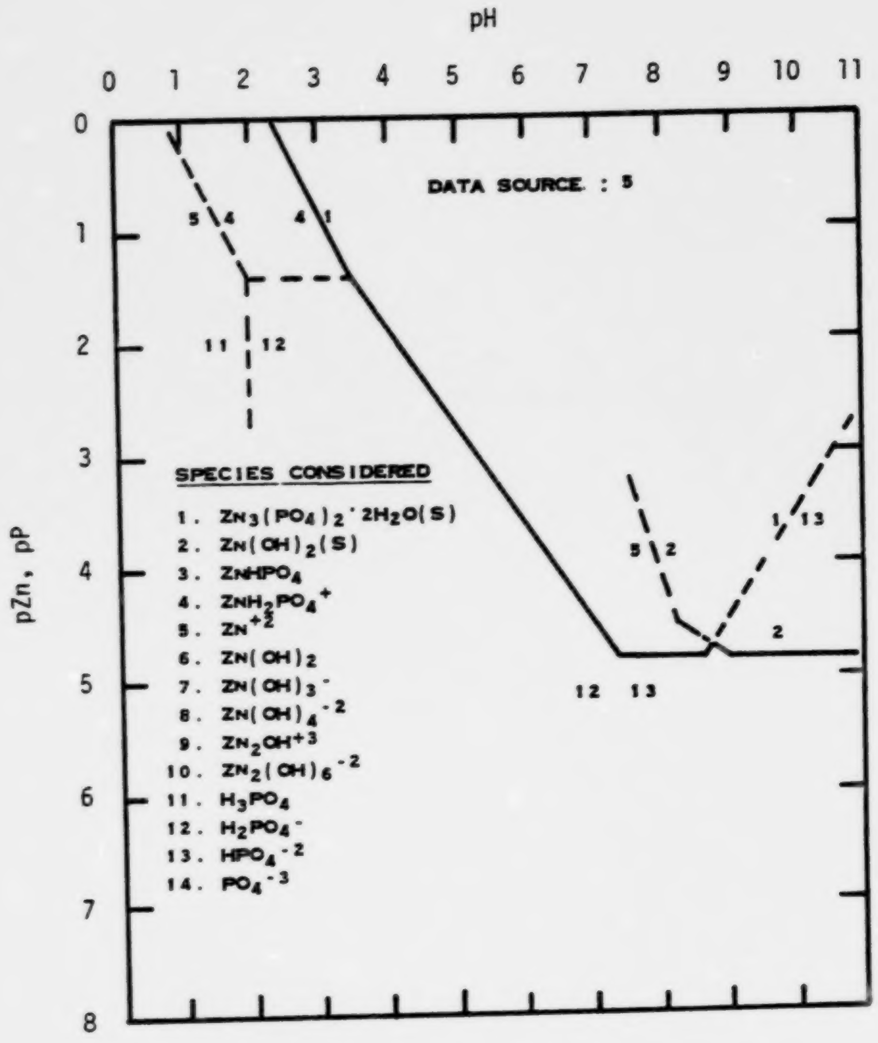


FIGURE 3. ZINC PHOSPHATE STABILITY DIAGRAM FOR THE ZINC-PHOSPHATE-WATER SYSTEM (7).

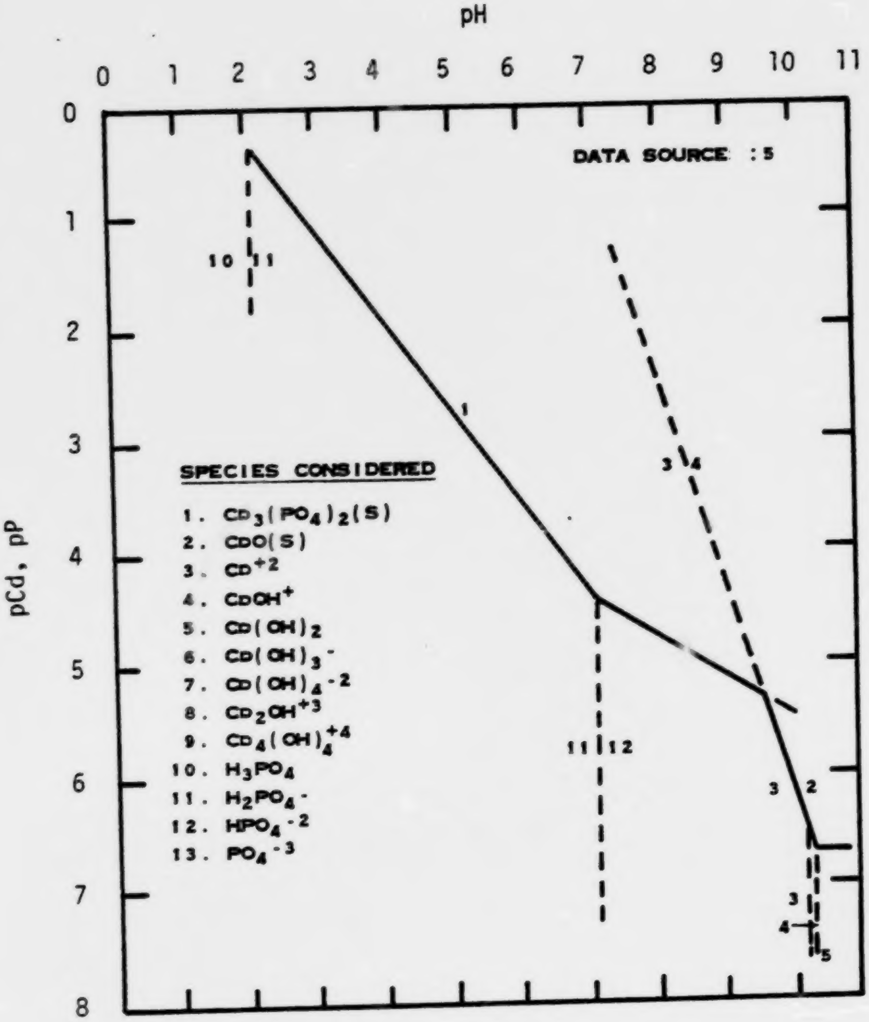


FIGURE 4. CADMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CADMIUM-PHOSPHATE-WATER SYSTEM (7).

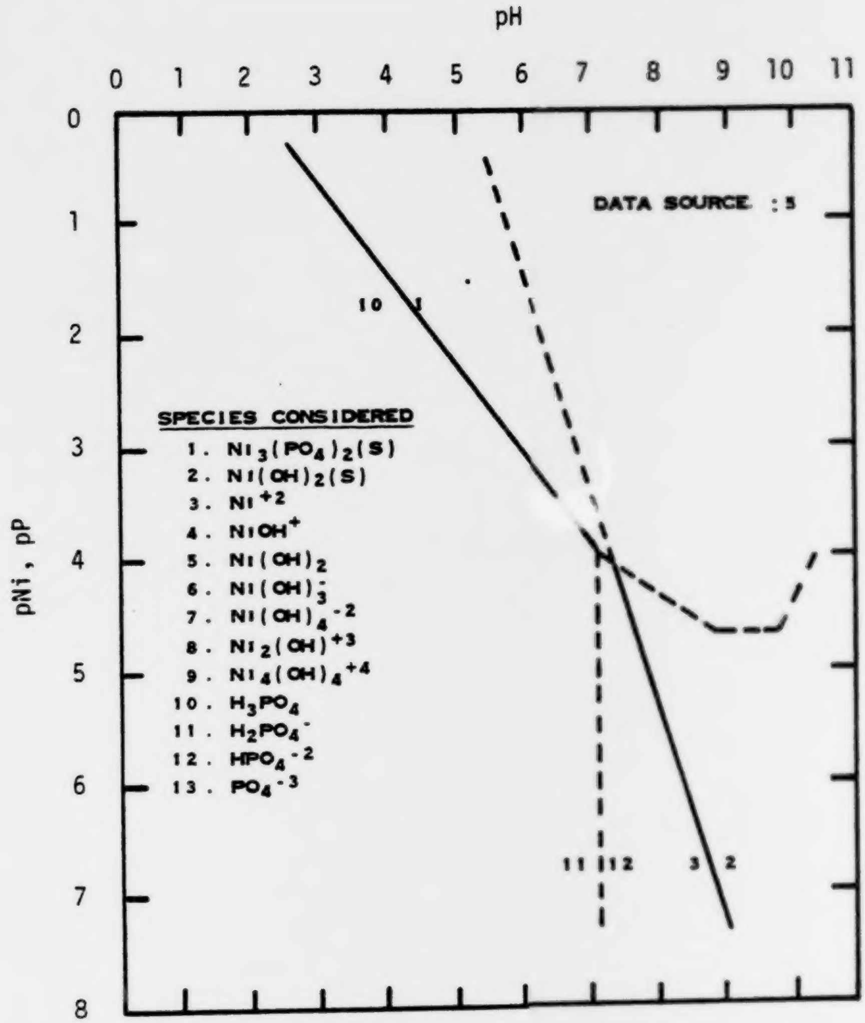
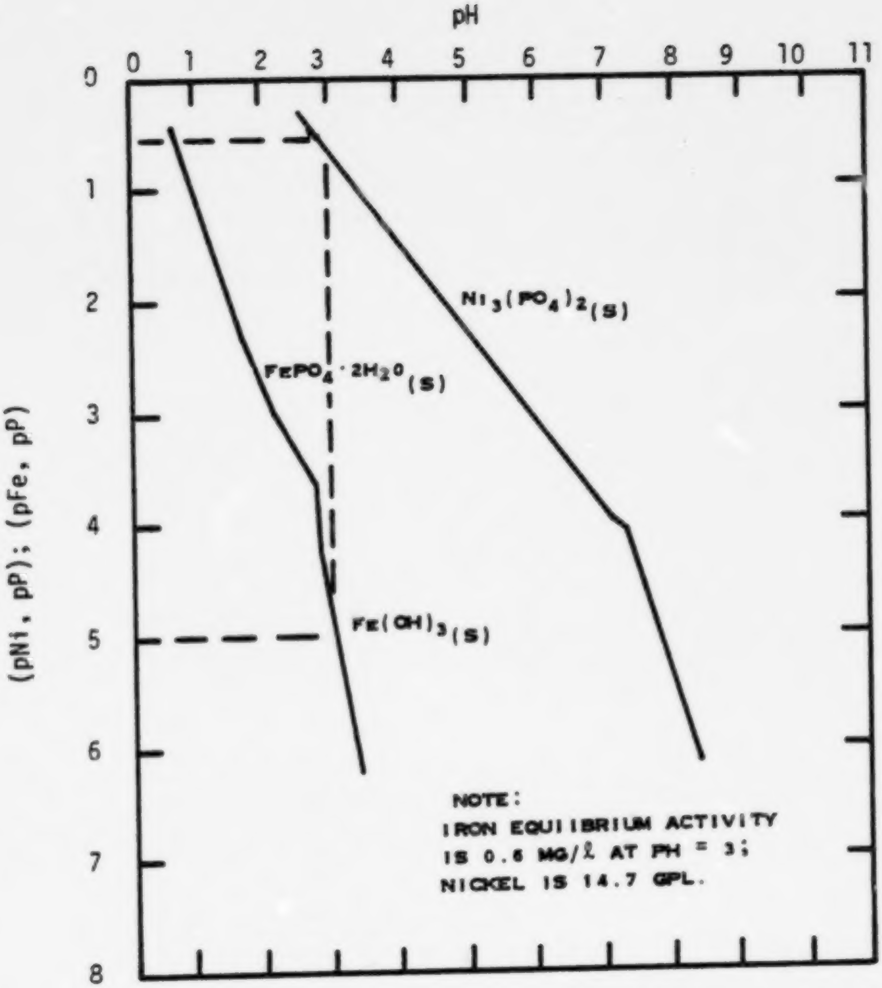


FIGURE 5. NICKEL PHOSPHATE STABILITY DIAGRAM FOR THE NICKEL-PHOSPHATE-WATER SYSTEM (7).



NOTE:
IRON EQUILIBRIUM ACTIVITY
IS 0.6 MG/ℓ AT PH = 3;
NICKEL IS 14.7 GPL.

FIGURE 6. IRON REMOVAL FROM NICKEL BY PHOSPHATE PRECIPITATION (7).

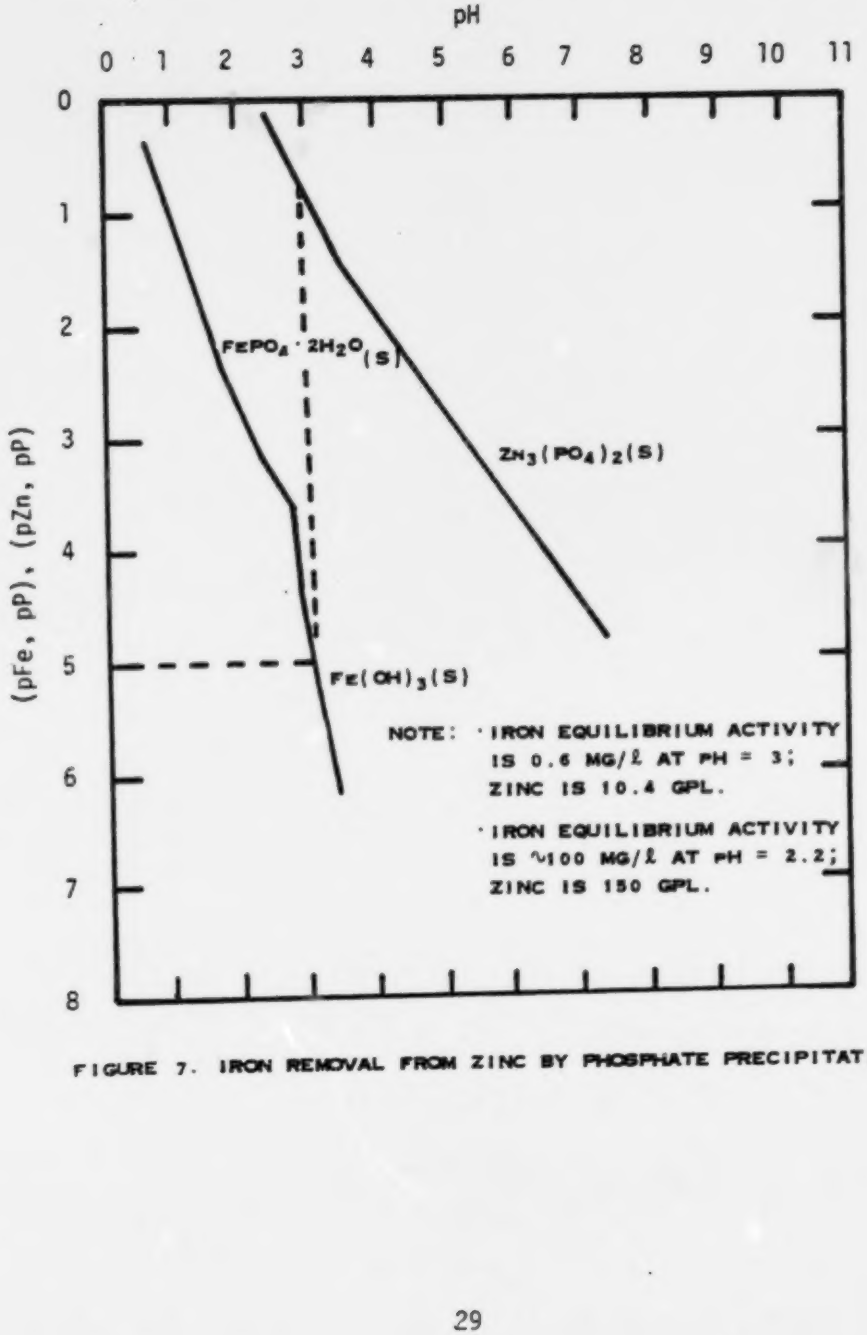


FIGURE 7. IRON REMOVAL FROM ZINC BY PHOSPHATE PRECIPITATION(7).

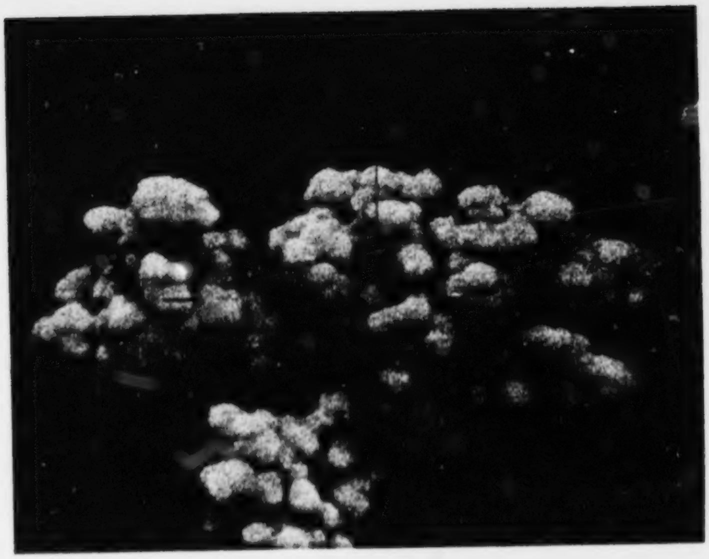


FIGURE 8. FERRIC PHOSPHATE PRECIPITATED FROM A MIXED METAL SOLUTION (1000X).

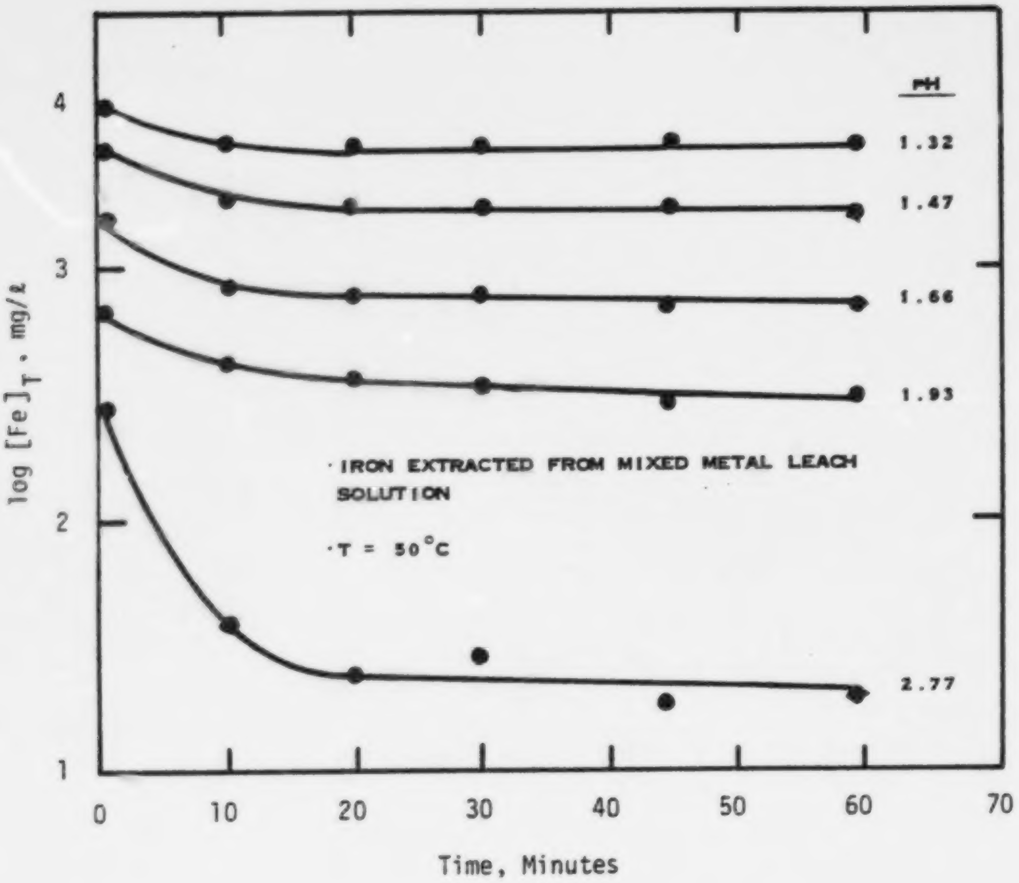


FIGURE 9. THE RATE OF PRECIPITATION OF FERRIC PHOSPHATE FROM A SULFATE BEARING SOLUTION (7).

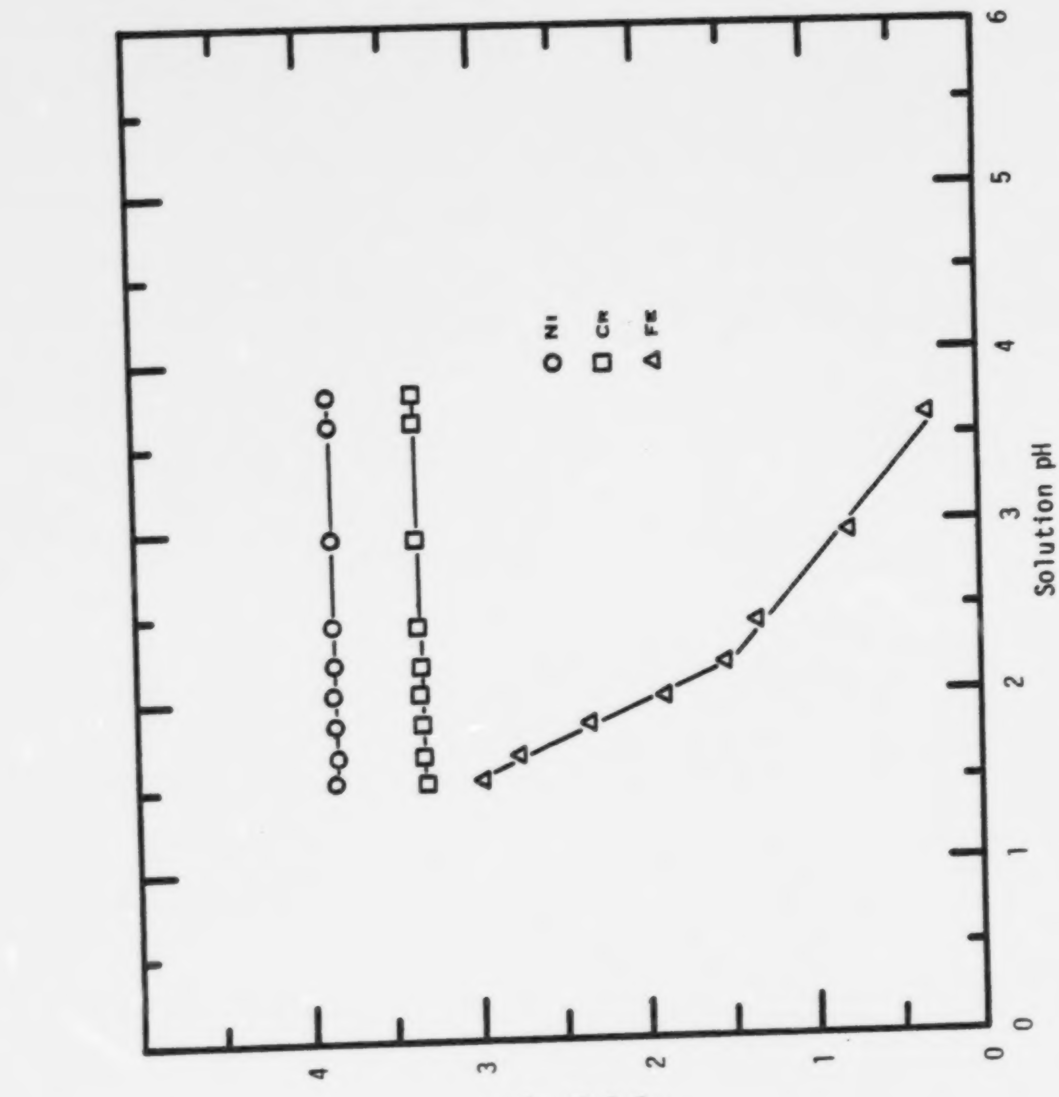


FIGURE 10. SELECTIVE REMOVAL OF IRON FROM CHROMIUM AND NICKEL AT ROOM TEMPERATURE (5).

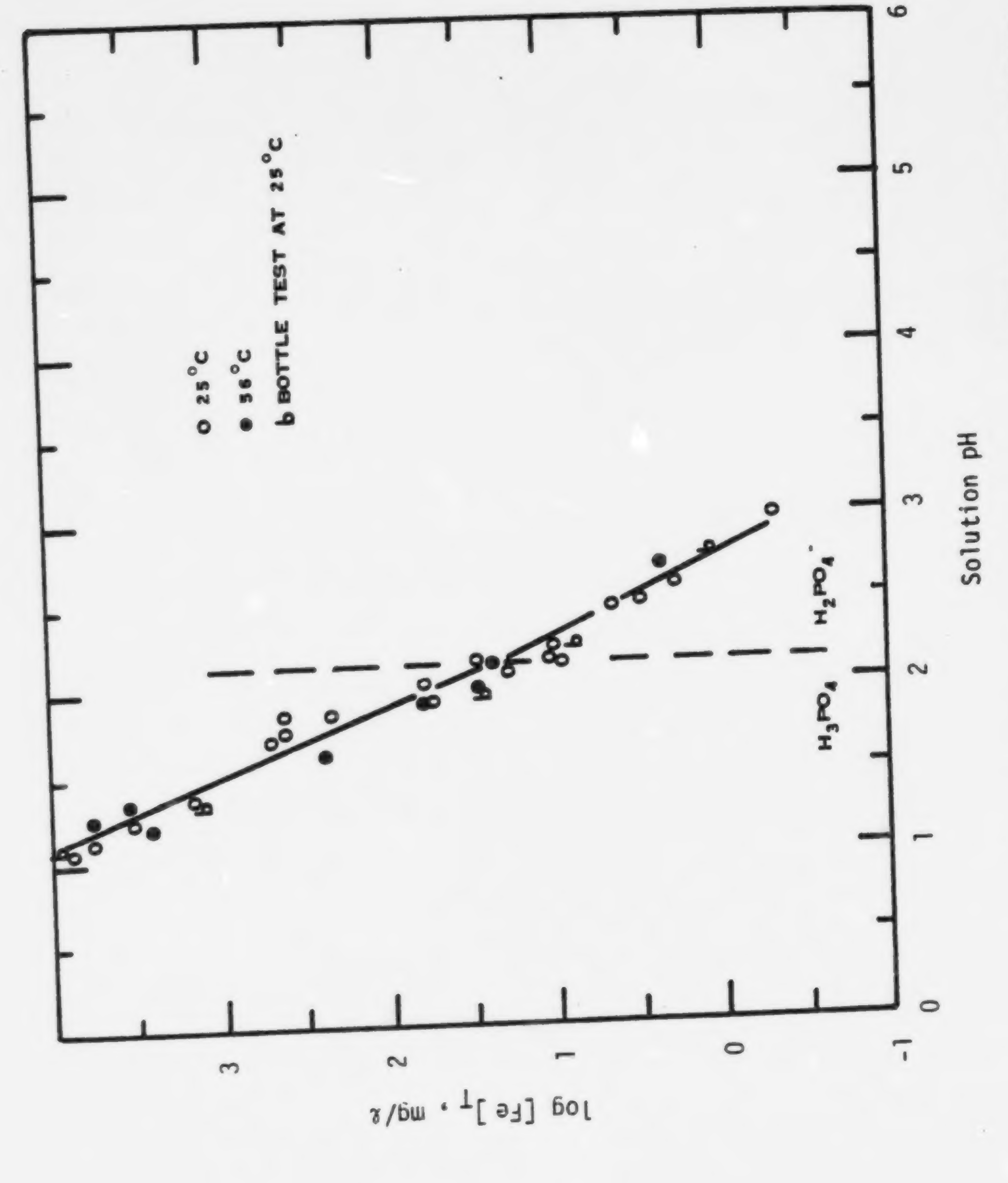


FIGURE 11. FERRIC PHOSPHATE PRECIPITATION FROM A CHLORIDE BEARING SOLUTION AT 25°C AND 56°C (7).

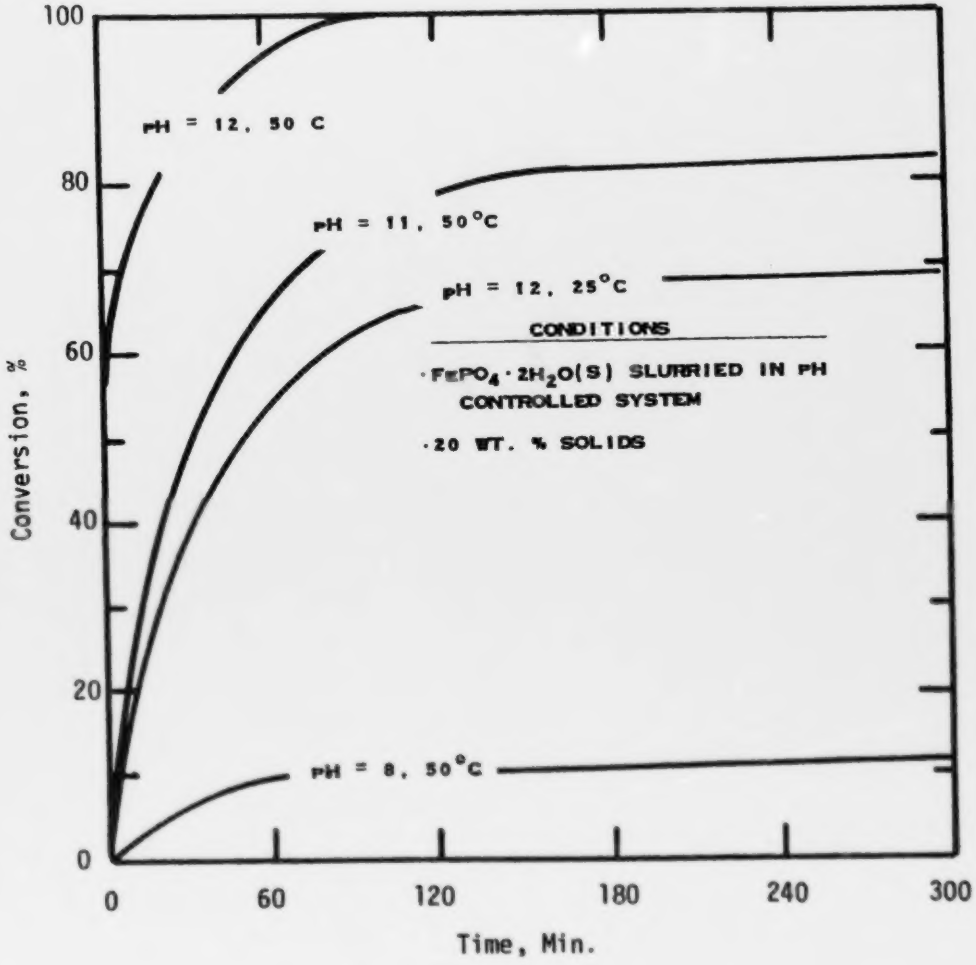


FIGURE 12. THE RATE OF CONVERSION OF FERRIC PHOSPHATE TO FERRIC HYDROXIDE AS A FUNCTION OF PH AND TEMPERATURE (7).

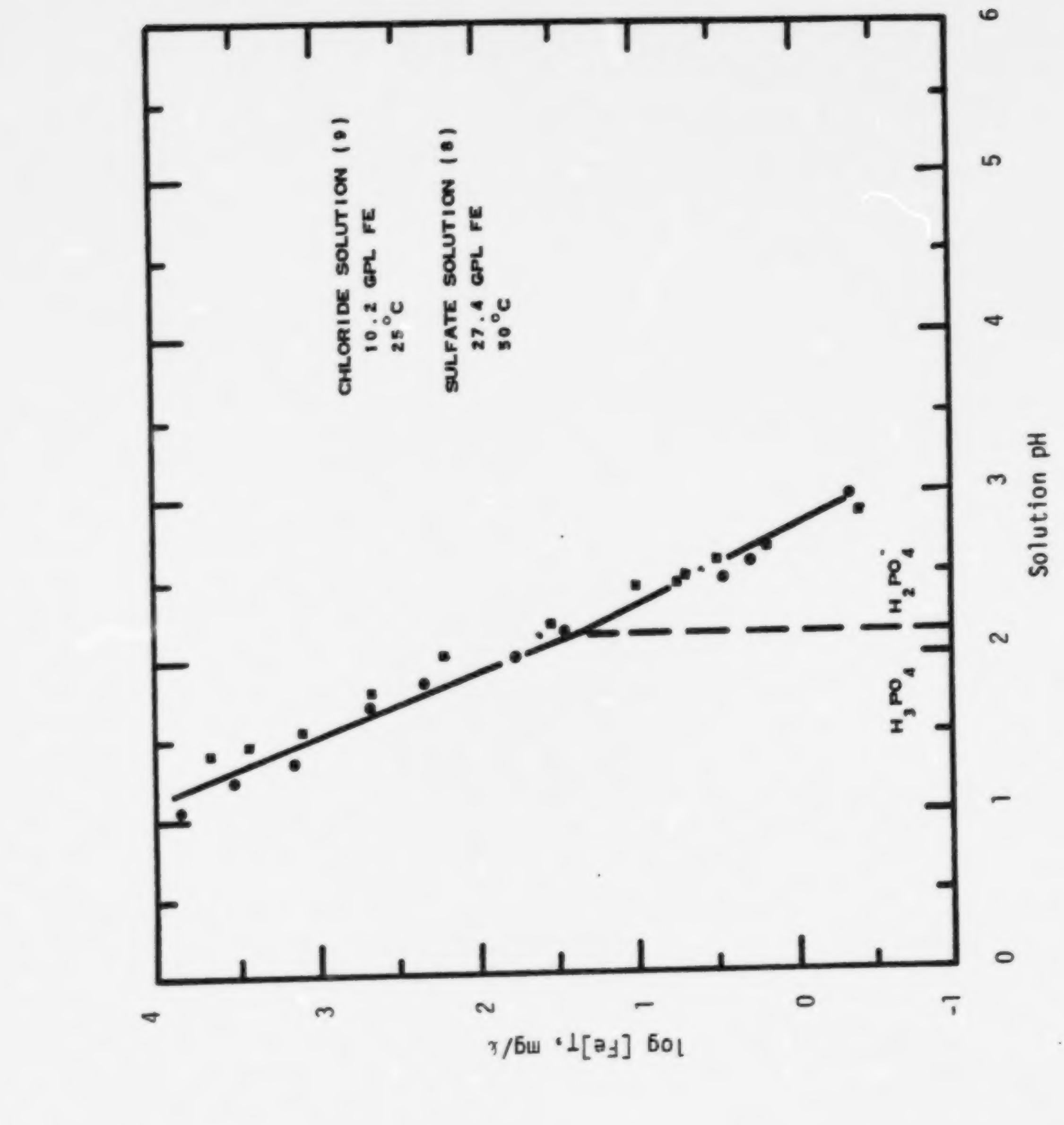


FIGURE 13. FERRIC PHOSPHATE PRECIPITATION FROM A CHLORIDE AND A SULFATE SOLUTION (5)

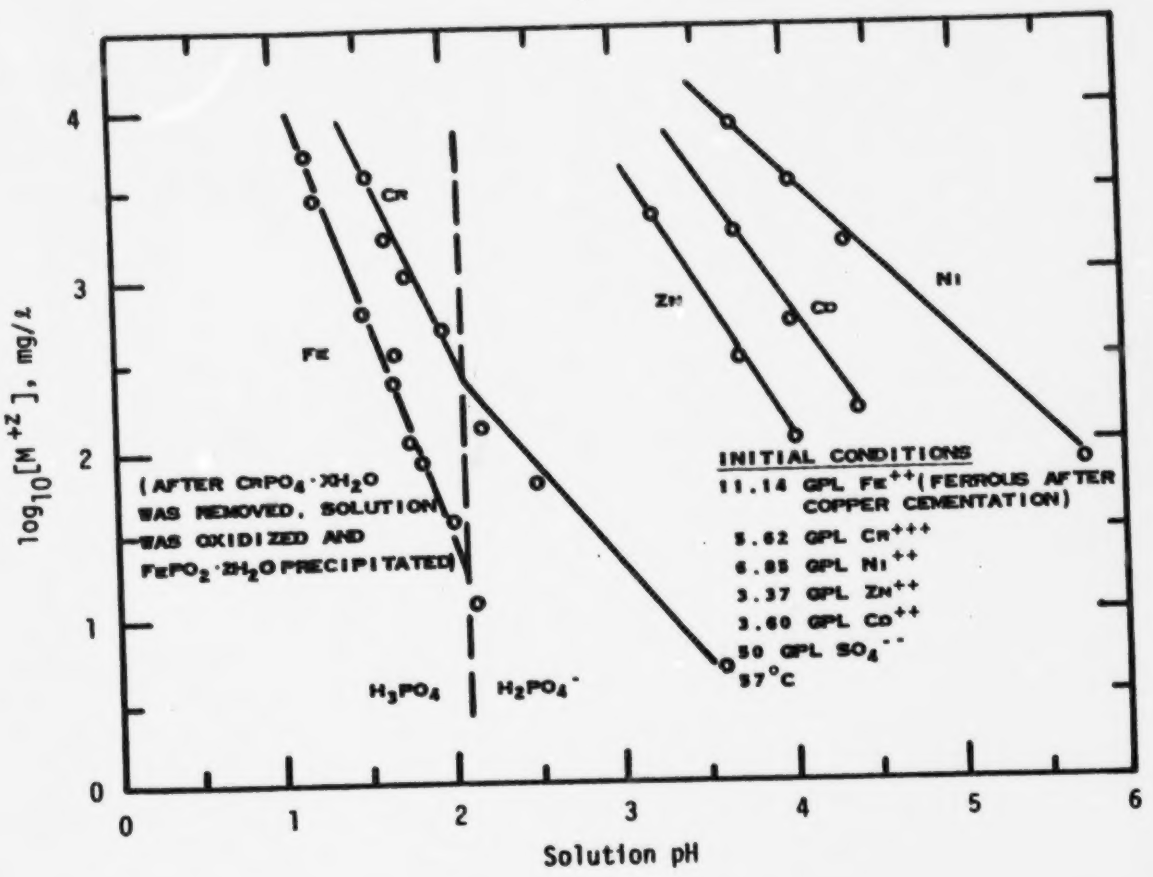


FIGURE 14. SELECTIVE REMOVAL OF CHROMIUM AND IRON FROM DIVALENT CATIONS IN ELECTROPLATING SLUDGE LEACH SOLUTIONS (7).

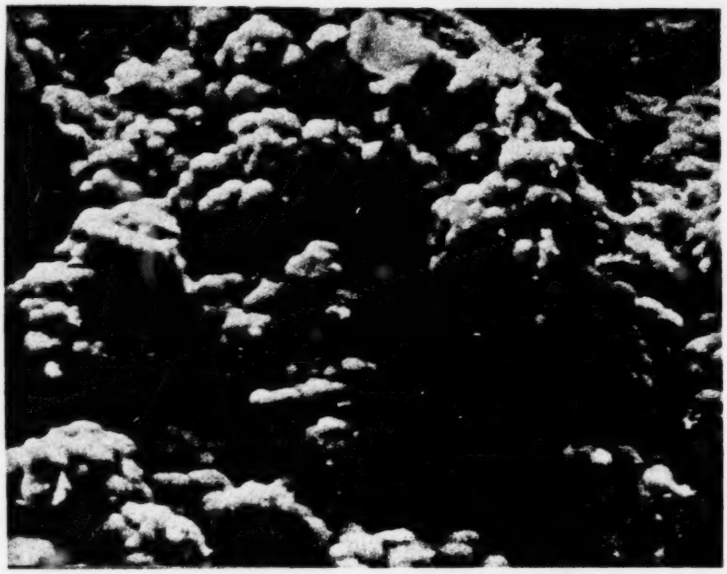


FIGURE 15. CHROMIUM PHOSPHATE PRECIPITATED FROM A MIXED METAL SOLUTION (1000X).

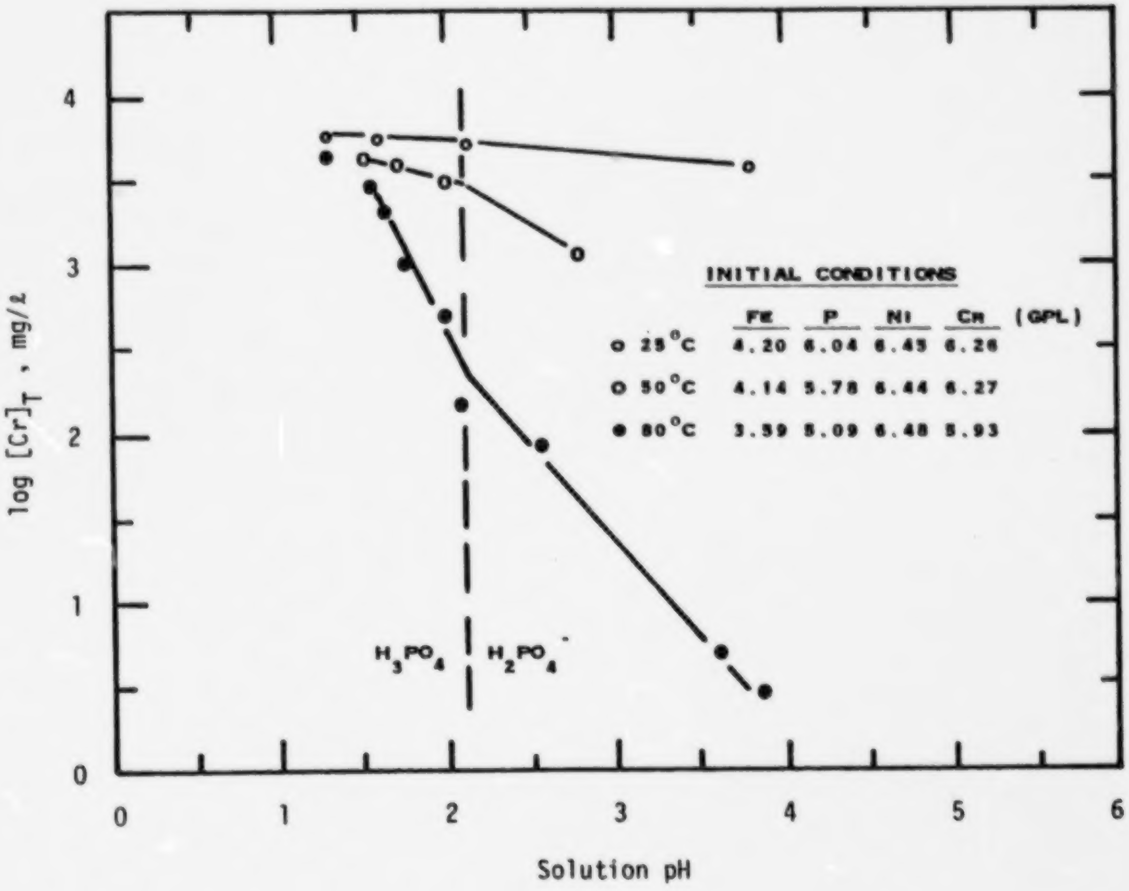


FIGURE 16. INFLUENCE OF TEMPERATURE ON CHROMIUM PHOSPHATE PRECIPITATION FROM A MIXED METAL SOLUTION (7).

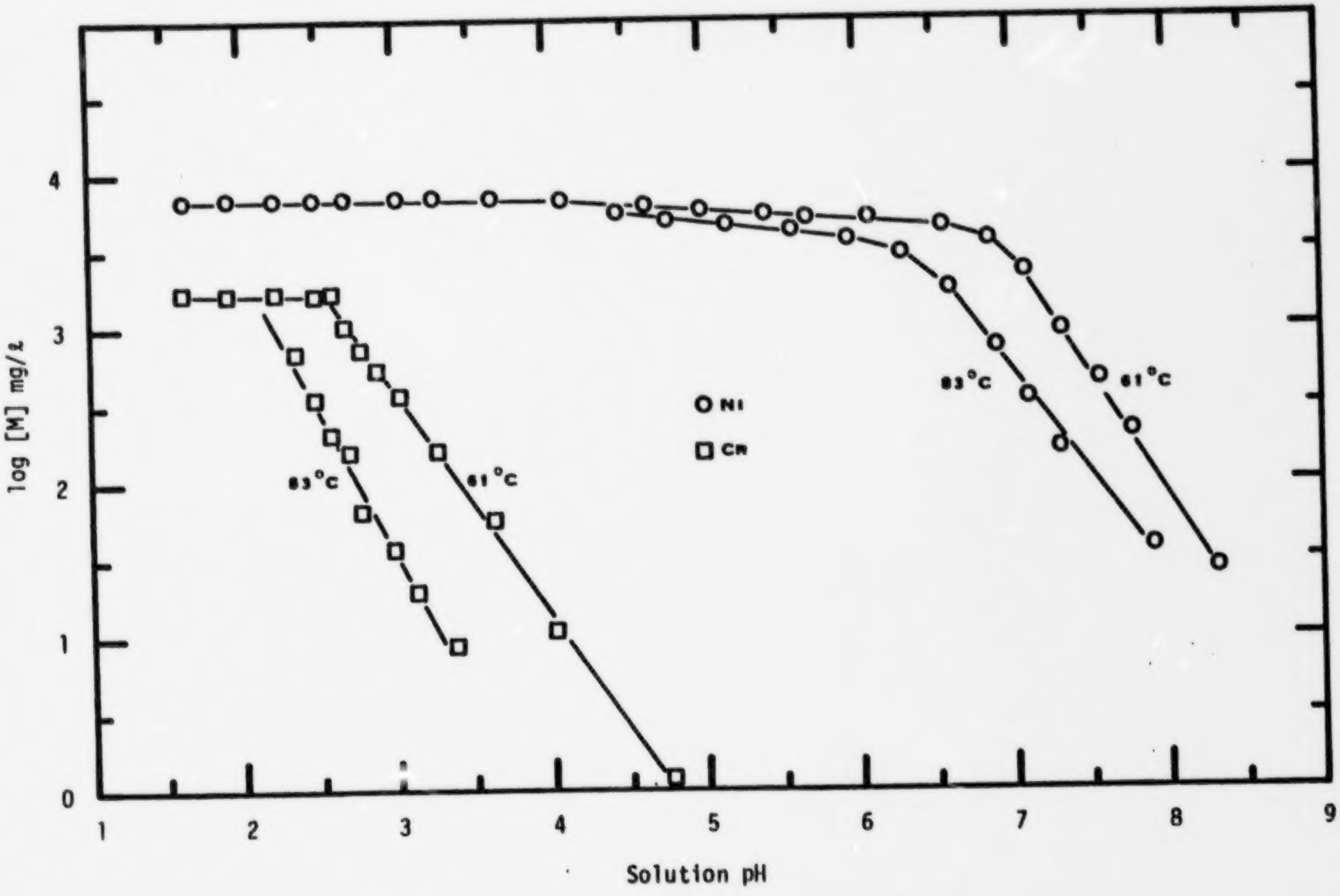


FIGURE 17. SELECTIVE SEPARATION OF CHROMIUM AND NICKEL (5).

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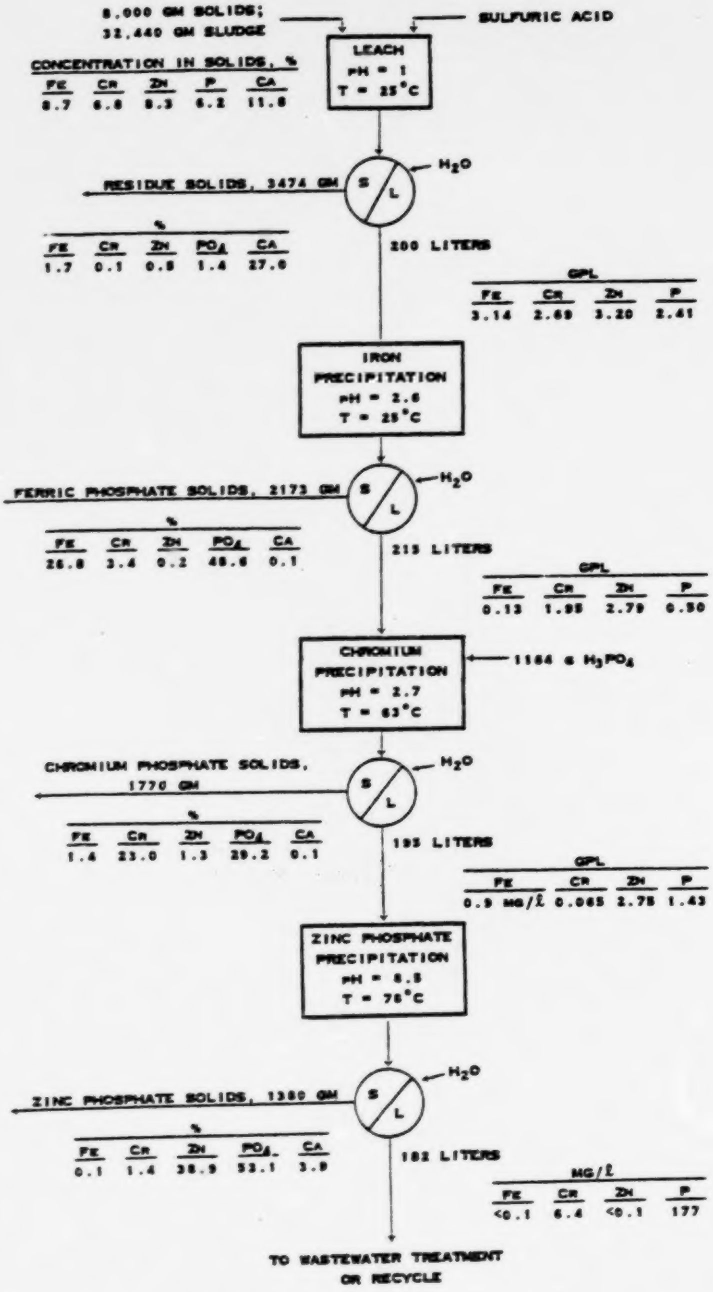
8,000 GM SOLIDS;
32,440 GM SLUDGE
SULFURIC ACID
CONCENTRATION IN SOLIDS, %
FE CR ZN P CA
8.7 6.8 8.3 6.2 11.8
LEACH
pH = 1
T = 25°C
H₂O
RESIDUE SOLIDS, 3474 GM
S
L
%
FE CR ZN PO₄ CA
1.7 0.1 0.5 1.4 27.0
200 LITERS
GPL
FE CR ZN P
3.14 2.69 3.20 2.41
IRON
PRECIPITATION
pH = 2.6
T = 25°C
H₂O
FERRIC PHOSPHATE SOLIDS, 2173 GM
S
L
%
FE CR ZN PO₄ CA
26.8 3.4 0.2 48.6 0.1
215 LITERS
GPL
FE CR ZN P
0.13 1.95 2.79 0.50
CHROMIUM
PRECIPITATION
pH = 2.7
T = 63°C
1164 G H₃PO₄
H₂O
CHROMIUM PHOSPHATE SOLIDS,
1770 GM
S
L
%
FE CR ZN PO₄ CA
1.4 23.0 1.3 29.2 0.1
195 LITERS
GPL
FE CR ZN P
0.9 MG/ℓ 0.065 2.75 1.43
ZINC PHOSPHATE
PRECIPITATION
pH = 8.5
T = 75°C
H₂O
ZINC PHOSPHATE SOLIDS, 1380 GM
S
L
%
FE CR ZN PO₄ CA
0.1 1.4 38.9 53.1 3.9
182 LITERS
MG/ℓ
FE CR ZN P
<0.1 6.4 <0.1 177
TO WASTEWATER TREATMENT
OR RECYCLE

FIGURE 18. FLOWSHEET FOR THE SEPARATION OF FE-CR-ZN BY PHOSPHATE PRECIPITATION.

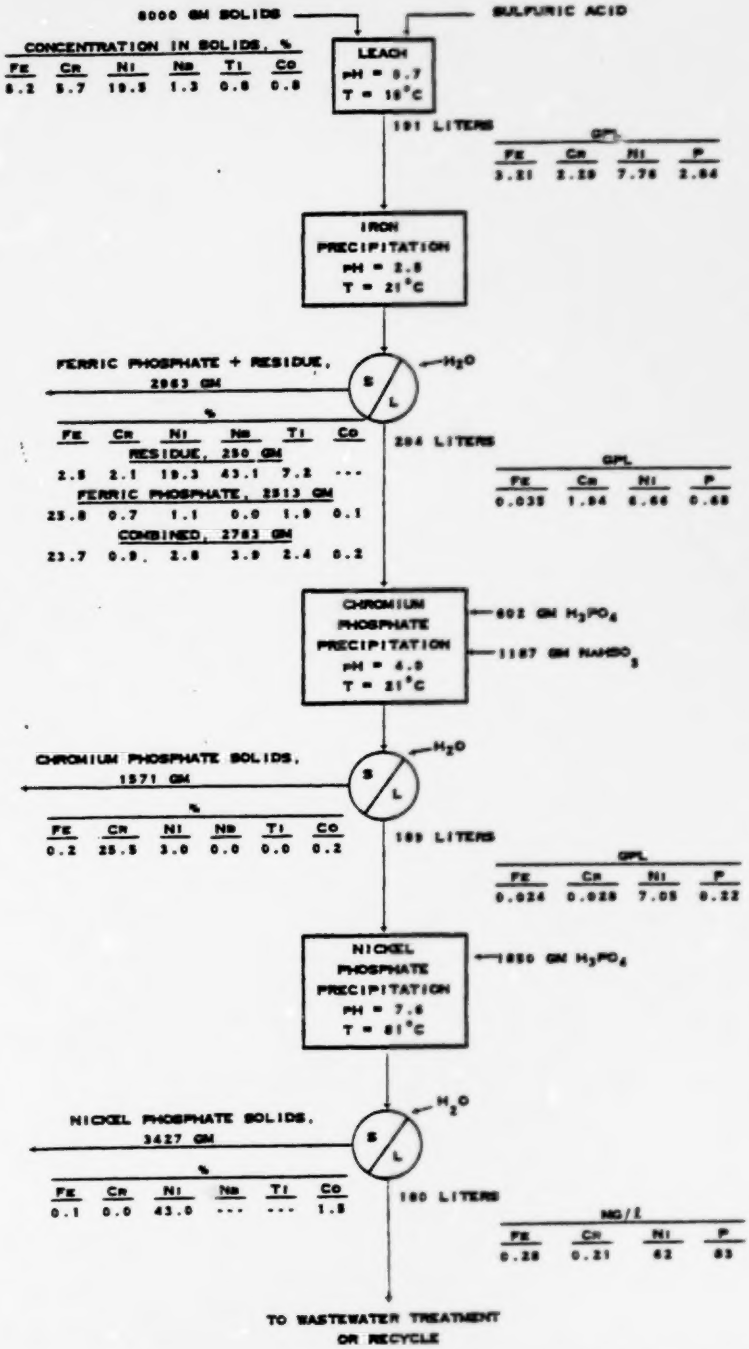
8000 GM SOLIDS
SULFURIC ACID
CONCENTRATION IN SOLIDS, %
FE CR NI NB TI CO
8.2 5.7 19.5 1.3 0.8 0.8
LEACH
pH = 0.7
T = 19°C
191 LITERS
GPL
FE CR NI P
3.21 2.29 7.76 2.84
IRON PRECIPITATION
pH = 2.5
T = 21°C
FERRIC PHOSPHATE + RESIDUE, 2963 GM
H_2O
S
L
%
FE CR NI NB TI CO
RESIDUE, 250 GM
2.5 2.1 19.3 43.1 7.2 ---
FERRIC PHOSPHATE, 2513 GM
25.8 0.7 1.1 0.0 1.9 0.1
COMBINED, 2763 GM
23.7 0.9 2.8 3.9 2.4 0.2
204 LITERS
GPL
FE CR NI P
0.035 1.94 6.66 0.68
CHROMIUM PHOSPHATE PRECIPITATION
pH = 4.0
T = 21°C
602 GM H_3PO_4
1187 GM $NaHCO_3$
CHROMIUM PHOSPHATE SOLIDS, 1571 GM
H_2O
S
L
%
FE CR NI NB TI CO
0.2 25.5 3.0 0.0 0.0 0.2
189 LITERS
GPL
FE CR NI P
0.024 0.028 7.05 0.22
NICKEL PHOSPHATE PRECIPITATION
pH = 7.6
T = 81°C
1850 GM H_3PO_4
NICKEL PHOSPHATE SOLIDS, 3427 GM
H_2O
S
L
%
FE CR NI NB TI CO
0.1 0.0 43.0 --- --- 1.5
180 LITERS
MG/L
FE CR NI P
0.28 0.21 62 83
TO WASTEWATER TREATMENT OR RECYCLE

FIGURE 19. FLOWSHEET FOR THE SEPARATION OF FE-CR-NI BY PHOSPHATE PRECIPITATION

TABLE 1. FILTERABILITY OF PHOSPHATE SOLIDS (7)

Conditions	Filterability Resistance, cm/g
$FePO_4 \cdot 2H_2O$ precipitated from 150 gpl Zn, SO_4 bearing solution, 50°C	
. pH Scan	4.01E09
. seed added	5.60E09
. product washed	4.10E09
$FePO_4 \cdot 2H_2O$ precipitated from SO_4 bearing solution, 80°C	7.30E09
$FePO4 \cdot 2H_2O$ precipitated from SO_4 bearing solution, 50°C, reslurried	4.24E09
Potassium Jarosite precipitated at pH=1.8, 90°C	7.44E09
Ferric Hydroxide precipitated at pH=3, 25°C	1.85E11

TABLE 2. PRODUCTS FROM TWO LARGE SCALE TESTS

Products	Solids, gm	Element Composition, %								
		Fe	Cr	Zn	Ni	Ca	PO_4	Nb	Ti	Co
Fe-Cr-Zn (Starting Solids)	8000	8.67	6.85	8.29	-	11.83	19.49	-	-	-
Leach Residue	3474	1.69	0.13	0.48	-	26.97	1.36	-	-	-
Ferric Phosphate	2173	26.75	3.39	0.15	-	0.05	48.63	-	-	-
Chromium Phosphate	1771	1.38	21.41	1.28	-	0.14	29.21	-	-	-
Zinc Phosphate	1230	0.09	1.40	33.88	-	3.93	53.05	-	-	-
Fe-Cr-Ni (Starting Solids)	8000	8.20	5.73	-	19.49	-	-	1.33	0.83	0.80
Leach Residue Plus Ferric Phosphate	2763	23.67	0.87	-	2.79	0.76	46.61	3.86	2.39	0.24
Chromium Phosphate	1571	0.19	25.53	-	2.99	0.92	48.82	0.01	0.02	0.18
Nickel Phosphate	3427	0.06	0.02	-	43.04	1.46	43.37	-	-	1.54

TABLE 3. EP TOXICITY TEST RESULTS

System	Analyses of Leach Solution from Extraction, mg/liter						
	Fe	Cr	Zn	Ni	Ca	Al	Nb
Fe-Cr-Zn							
Leach Residue	1.64	1.66	3.44	-	-	-	-
Ferric Phosphate	0.86	0.14	0.37	-	1.91	0.28	-
Fe-Cr-Ni							
Leach Residue + Ferric Phosphate	0.19	<0.00	0.32	5.51	1.40	<0.00	<0.00

Note: EPA designated concentration of chromium for characteristic toxicity is 5.0 mg/liter. Other metals are not listed (11).

TABLE 4. ELEMENTAL DISTRIBUTION FOR TWO LARGE SCALE TESTS

System	Element Distribution, %						
	Fe	Cr	Zn	Ni	Ca		
Fe-Cr-Zn							
Leach Residue	8.5	0.8	2.6	-	99.0		
Ferric Phosphate	83.8	13.4	0.5	-	0.1		
Chromium Phosphate	3.5	74.3	3.5	-	0.2		
Zinc Phosphate	0.2	3.1	80.9	-	5.1		
Final Solution	<0.0	0.2	<0.0	-	-		
Fe-Cr-Ni					Nb	Ti	Co
First Solids							
Metallic Residue	1.0	1.2	-	3.1	101.3	28.1	0.0
Ferric Phosphate	99.0	4.1	-	1.8	0.0	74.6	7.9
Chromium Phosphate	0.4	87.6	-	3.0	-	-	4.9
Nickel Phosphate	0.5	0.2	-	94.6	-	-	80.3
Final Solution	<0.0	<0.0	-	0.7	-	-	-

TABLE 5. METAL VALUE RECOVERY BY SULFURIC ACID DISSOLUTION

	Element Extracted, %				
	Fe	Cr	Zn	Ca	P
Fe-Cr-Zn	90.0	98.9	96.4	0,6	97.2
	Fe	Cr	Ni	Nb	Ti
Fe-Cr-Ni	93.5	95.9	95.0	0.0	74.6

TABLE 6. EXAMPLES OF METAL VALUE RECOVERY BY SULFURIC ACID DISSOLUTION (2)

Condition	Element Extracted, %						
	Fe	Cu	Zn	Ni	Cr	Cd	Al
100 grams	92.0	93.7	95.9	95.9	95.9	93.0	87.1
1000	95.8	94.3	94.2	85.0	96.7	97.0	96.0
22,700	65.0	92.0	96.9	92.1	92.3	100.0	98.9
50,600	92.0	93.7	95.1	95.9	96.5	93.0	96.9

Note:
- All sludge samples were undried.
- Sulfuric acid added equivalent to 100% of solid weight.
- One-half hour, 40-50°C, pH = 1.5.

PLATING WASTE SLUDGE METAL RECOVERY

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Abstract

Army depot electroplating shops are facing increased costs for metal-bearing sludge disposal; metals extraction offers the potential for resource recovery and simplified sludge disposal. A sulfuric acid leach process can remove 99% of metal values from a synthetic hydroxide sludge; lime treatment renders the filter cake non-hazardous to EP testing. The acid leach extract is treated by selected sulfide precipitation at controlled pH for metals separation followed by solvent extraction for further recovery.

Background

There are 23 Army installations engaged in metal plating operations employing a variety of techniques to treat the resulting wastewater. While some sites are recovering metals for reuse in plating baths, a majority still find it advantageous to precipitate the metals and discharge the wastewater. Sludges are collected in clarifiers in many of the facilities and are variously treated by gravity thickening and then dewatered by pressure filters, vacuum filters, lagoons, and sludge drying beds. Once the sludge has been dewatered as much as practical, it is either incinerated, landfilled, or contracor hauled, but in most cases it is classified as hazardous, so that options for landfilling are limited.

These sludges contain metals that have potential economic value and in some cases strategic value. Separation and recovery will become advantageous in the future, and so a study[1] was conducted to review current state-of-the-art in metal recovery from plating waste sludges and identify any promising new techniques for which the chemical mechanisms occurring in a separation procedure can be experimentally determined for a typical sludge.

Under contract, AMAX Extractive Research and Development, Inc. personnel examined a number of processes which could lead to a potential sludge treatment and metal recovery process. An extensive database was assembled and reviewed. Prior studies of military metal finishing waste treatment established a typical composition for the sludge and for a representative synthetic sludge containing metal hydroxides.[2,3]

A detoxification and recovery process should be sufficiently flexible to treat a mixture of elements at various stages of aging. The secondary sludge remaining from a metal recovery operation must pass the U.S. Environmental Protection Agency's Extraction Procedure (EP) leach test[4] for the toxic metals cadmium and chromium.

Development of the Synthetic Sludge

Since electroplating wastes originate primarily from rinse solutions rather than plating bath disposal, the synthetic sludge was produced by liming dilute solutions formulated to produce a typical sludge. Rinse baths generally contain sulfates, and liming these solutions will form a significant amount of gypsum as a coprecipitated compound along with the metal hydroxides. In addition, iron frequently occurs in any sludge to be treated[3], so that after recovery of the valuble constituents from sludges, the secondary sludge will consist primarily of gypsum and iron hydroxide compounds.

The hydroxide sludge was formed by lime treatment of dissolved metal sulfates to pH 9 to produce a sludge of the approximate composition:

Compound	% Dry Weight
$Cd(OH)_2$	1
$Cr(OH)_3$	10
$Cu(OH)_2$	7
$Fe(OH)_2$	7
$Ni(OH)_2$	7
$Zn(OH)_2$	7
$CaSO_4$	61
Total	100

Potential Processes

The synthetic sludge was the starting point for a test program aimed at determining critical steps in detoxification and recovery processes. The objective of such processes is to minimize the volume of secondary sludges and render them inert to the EP leach test for hazardous substances. Three leaching operations were identified:

Ammonia leach followed by acid or caustic leach
Caustic leach
Acid leach

The sulfuric acid leach procedure is reported[5] to yield the highest extraction of heavy metal species. Since the residual solids from a sulfuric acid leach are, after liming, apt to be relatively inert to the conditions of the EP leach test, this process was chosen for laboratory evaluation as a metal recovery technique. The sulfuric acid leach would have the following potential advantages:

1. Sulfuric acid is an inexpensive reagent and can be recovered by distillation if necessary.

2. The sulfuric acid leach has no effect on the gypsum in the sludge.

3. Heat released by dilution of concentrated sulfuric acid and by reaction with basic hydroxides accelerates the leach kinetics without additional heating required.

4. The subsequent recovery schemes require an acidic pH.

5. Stagewise leaching with countercurrent flow of solids and acid can be employed to minimize acid addition and maximize washing of the gypsum cake.

Design of the Research Test Plan

A test program was developed consisting of several steps:

1. Preparation, aging, and characterization of the metal hydroxide sludges.

2. Acid leaching of the sludges and characterization of the residual filter cake.

3. Extraction testing on the filter cakes.

4. Separation of metals by sulfide precipitation.

This test plan was designed to account for such concerns as (1) whether prior aging history of the sludge significantly affects the leach kinetics and recovery; (2) whether the residual gypsum cake can be made sufficiently inert as to be non-toxic and readily disposable; and (3) whether a sulfide process can easily separate heavy metals from chromium.

For metals analysis, aqueous solution samples were subjected to inductively coupled plasma analysis or flame atomic absorption.

Preparation and Aging of Sludges

A stock solution of reagent grade metal sulfates was prepared and carefully reacted with a 10% lime slurry to avoid formation of inhomogenous masses of precipitate. The sludge was allowed to settle, and the clear solution was decanted and analyzed. The sludge was analysed and divided into three portions. The first was treated promptly by the acid leach procedure, the second was held for one week at 65°C, and the third was aged for 6 weeks at room temperature. This third sludge is probably more characteristic of actual plating sludges which would occur in a natural environment.

The clear decant solution remaining from the lime precipitation gave the following analysis:

	Parts per million of metals					
Cu	Cr	Ni	Fe	Cd	Zn	Ca
0.10	0.055	0.014	0.03	0.16	0.042	665

Leaching of Sludges and Characterization of Leach Residues

The objective of the leach process is to maximize the recovery of the metals and produce a secondary leached filter cake which has a low solubility of heavy metals, expecially cadmium and chromium. The variously aged portions of metal hydroxide sludges were suspended in deionized water and concentrated sulfuric acid was added gradually with stirring until the solution reached a pH of 1.5. After 90 minutes of reaction time the solution was filtered and the filter cake washed with 0.1 normal sulfuric acid and set aside for the subsequent EP leaching test.

Analysis of the filter cakes showed that the acid leach removed close to 100% of each of the metals except cadmium which was nearer to 98%. The sludge that was heated for 1 week at 65°C showed that the accelerated aging made the sludge slightly more refractory to leaching.

		Percent Extracted					
Sludge type	% Solids	Cu	Cr	Ni	Fe	Cd	Zn
No Aging	62.5	99.4	99.4	99.7	99.3	97.5	99.5
7-Day Aging	93.3	99.2	99.1	99.4	99.3	97.3	99.4
6-Week Aging	87.0	99.6	99.6	99.7	99.7	98.2	99.7

Extraction Testing on Filter Cakes from Sulfuric Acid Leaching

The EP leach test was performed to determine the effect of leaching, washing, and added lime on the solubility of the filter cake in a simulated environmental exposure. In this procedure, 100 grams of the filter cake are slurried in 1.6 liters of deionized water and the pH adjusted to 5.0 with 0.5N acetic acid. The suspension is mixed for 24 hours at 25°C and the solution analyzed for metals. Results of the EP leach testing showed:

	Parts per Million of metals					
Sludge type	Cu	Cr	Ni	Fe	Cd	Zn
No Aging	0.88	0.53	0.53	0.075	1.24	0.98
7-Day Aging	7.19	4.10	9.39	0.19	2.29	12.4
6-Week Aging	1.21	1.16	1.13	0.05	1.09	1.67
Limit *	-	0.50	-	-	0.10	-

* Limit equals maximum levels of heavy metals allowed in order for the sludge to be classified as non-hazardous.

An explanation for the higher concentration from the aged sludges may be that during syneresis, or aging, some trapping of heavy metals (either by chemisorption, mechanical occlusion, or lattice substitution) may occur. Photomicrographs show a difference in crystalline structure. As a result, the sulfuric acid leaches are not effective in removing all heavy metal constituents. However, during the 24-hour acetic acid treatment of the EP leach test, the trapped metals are solubilized.

One sample of the 6-week aged sludge was vigorously washed in a blender during the sulfuric acid leach procedure. This action apparently broke down the crystalling structure of the sludge allowing more complete washing out of the heavy metals. EP leach test results on this particular filter cake showed that lower concentrations were present.

	Parts per Million of Metals					
Sludge type	Cu	Cr	Ni	Fe	Cd	Zn
6-Week Aged	0.30	0.22	0.13	0.092	0.67	0.38

Two samples of the 6-week aged sludge were treated with solutions of hydrated lime while being slurried for the EP leach test. This had the effect of further lowering the concentration of metals which could be extracted by the EP leach test.

		Parts per Million of Metals					
Sludge type	Lime Addition	Cu	Cr	Ni	Fe	Cd	Zn
6-Week Aged	1:10	0.011	0.11	0.12	0.016	0.036	0.058
6-Week Aged	1:2.4	0.007	0.13	0.014	0.015	0.009	0.026

Separation of Metals by Sulfide Precipitation

Controlled addition of a sodium sulfide solution to the sulfuric acid leach liquors was conducted to bring about separation among the metals. To one liter of the leach solution, a stock solution of sodium sulfide, 29.5 grams per liter of sulfide ion, was added at a rate of two milliliters per minute at a temperature of 60°C for 300 minutes with continuous stirring and periodic sampling. As the quantity of sulfide increased, the pH gradually increased and certain metals precipitated from solution. The filtered precipitate was washed with 2 liters of deionized water which was returned to the leach liquor so that unreacted metals were returned to the solution.

A summary of the test results shows the effect of this procedure; copper, cadmium, and zinc are effectively separated from chromium, but nickel and iron are incompletely separated:

Milliequivalents of Sulfide Addition	Weight % Remaining in Solution					
	Cu	Cd	Zn	Ni	Fe	Cr
0	100	100	100	100	100	100
110	67.45	97.92	97.85	96.62	97.74	98.29
330	3.05	94.80	95.66	97.01	94.50	95.28
660	0.22	0.75	50.94	73.92	92.76	94.97
1100	0.11	0.49	0.97	29.56	86.40	91.09
1100 + Wash	0.23	0.64	2.59	34.72	94.92	99.03

Recovery of Chromium by Solvent Extraction

After sulfide precipitation to remove copper, cadmium, zinc, and some nickel, the treated solution will primarily contain chromium, iron, and the remaining nickel. By raising the pH, a chromium and iron precipitate will form while the nickel stays in solution. A solvent extraction process can effectively separate the chromium from the iron.

In a series of shakeout tests, separation was effected by the use of di-2-ethylhexyl phosphoric acid, 3,7-dimethyloctanal oxime, and Escaid 200. The iron concentrates in the organic phase while the chromium remains in the aqueous phase. The tests suggest that a multiple-stage countercurrent, continuous solvent extraction circuit would provide a high degree of separation.

Summary and Conclusions

Aging of metal plating sludges has little effect on the recovery of heavy metals by sulfuric acid leaching.

Sulfuric acid leaching of a prepared plating sludge is effective in short contact time, about 30 minutes, in effecting greater than 99 percent recovery of copper, chromium, nickel, zinc, and iron and greater than 97 percent recovery of cadmium in the leach liquor. Under the leaching conditions employed, rendering the residual filter cake into compliance as non-hazardous by the EP leach test was not possible.

However, the residual filter cake after sulfuric acid leaching can be made to meet non-hazardous criteria by blending 10 percent by weight of lime to the solids which are primarily calcium sulfate.

Sulfide precipitation under controlled pH on the sulfuric acid leach liquors is effective in separating copper and cadmium quantitatively as sulfides from the chromium which remain in the solution. Zinc is nearly quantitatively precipitated, but nickel and iron are only partially removed.

Further separation between iron and chromium is possible with a mixture of organic solvents.

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TREATMENT OF AQUEOUS METAL BEARING HAZARDOUS WASTES

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ABSTRACT

This paper describes the work being conducted at USEPA's Test and Evaluation Facility involving the treatment of metal finishing hazardous wastewaters. This work is part of a comprehensive program supporting the demonstration, testing and evaluation of treatment processes which have the potential to be utilized to meet the forthcoming requirements of the land disposal restrictions of the HSWA, 1984. A variety of unit treatment processes have been fabricated to offer BDAT (Best Demonstrated Available Technology) in treating hazardous, aqueous metal waste streams. These unit processes include lime precipitation, flocculation, clarification, sulfide precipitation, mixed media filtration, ion exchange, and granular activated carbon adsorption. The results of the first three test runs will be presented.

I. Introduction

The reauthorization of RCRA was passed on November 8, 1984, as the Hazardous and Solid Waste Amendments (HSWA). This legislation imposed new responsibilities on the handlers of hazardous wastes - including metal finishers and electroplaters. As a result of the HSWA, in 1985, the direct placement of noncontainerized liquid in landfills, surface impoundments and deep wells was prohibited. Other containerized material was significantly restricted. In fact, each hazardous waste stream (as defined) following pre-treatment would have to pass three tests before land disposal would be accepted: (1) paint filter for free moisture content, (2) the toxicity characteristics leaching procedure (TCLP), which is a limit imposed upon 54 organic compounds and 9 heavy metals, and (3) a pre-treatment standard which will be referred to as a Best Demonstrated Available Technology limit.

More than one treatment standard (or condition) may be set, based on such factors as the physical form or the chemical properties of the waste. Determination of these land disposal restrictions will be made incrementally, by thirds, for all listed hazardous wastes, by May 8, 1990. Land disposal prohibitions are effective immediately upon promulgation unless there is a postponement to the earliest date on which adequate alternative treatment, recovery or disposal capacity will be made available. Only case-specific petitions that successfully demonstrate "safe" disposal will be authorized until more permanent standards are in place.

Another significant responsibility imposed by the HSWA concerns small quantity generators. Now, large quantity generators are defined as those who generate more than 100 kg per calendar month. As a result, many more small quantity generators will be brought into the regulatory fold.

An estimated 7.9 billion gallons of metal-bearing wastes, 4.7 billion gallons of cyanide wastes, and 0.8 billion gallons of reactive wastes containing cyanides were generated in the U.S. in 1983.[1] Hazardous wastes which can be categorized as metal and cyanide-bearing wastes are included in each of the five source designations for hazardous wastes:[2]

D - Wastes which are hazardous because they exhibit a particular hazardous characteristic, e.g. TCLP, corrosivity, etc. (These streams would result directly from plating process lines);

F - Wastes from non-specific sources, e.g. sludges from pre-treatment of spent process wastewaters and plating process lines;

K - Wastes from specific sources, (industrial discharges); e.g. pigments and dyes;

P - Acutely hazardous constituents as commercial or off-specification chemicals and intermediaries; and

U - Toxic constituents (same as 'P' criteria).

The majority of metal/cyanide wastes generated in this country are characteristic toxic metals (D) and (F) wastes resulting from electroplating and metal treating processes. The distribution of these wastes is shown in Table 1. Regulations will be targeting both pre-treatment operations (in-plant) and commercial facilities (local and/or centralized) as treatment standards are established.

TABLE 1. Generated Waste Distribution[3]

Hazardous Waste Group	Metals: Annual Volume (M gal.)	Metals: % of Total Metals	Metals: No. of Generators	Cyanides: Annual Volume (M gal.)	Cyanides: % of all CN	Cyanides: No. of Generators
D wastes	3,685	46.9	3,860	est. 750	--	n/a
F wastes	3,920	49.9	2,091	3,920	83.0	2,091
K wastes	219	2.8	402	572	12.1	10
P wastes	28.3	0.36	405	226	4.8	800
U wastes	5.2	0.07	365	3.9	0.08	306
Total	7,858		6,586	4,723		2,781

The purpose of this experimental work is to demonstrate BDAT for aqueous metal treatment and recovery processes. The results of these studies will help support the land disposal restrictions program. Major objectives will focus on:

(1) Evaluating heavy metal reduction and concentration of process residuals from selected metal waste streams;

(2) Determining to what extent organic (complexing) interferences affect metals treatment;

(3) Characterizing treatment residuals for specific unit treatment processes, (solid, liquid, and gaseous residuals), and

(4) Providing BDAT data for rule challenges and petitions.

To accomplish these objectives, a versatile system composed of unit processes reflecting both conventional and advanced technologies has been designed and fabricated. These unit processes are arranged to provide maximum flexibility for studying the best mix/match of process technology to waste stream for a variety of aqueous metal wastes.

The results presented in this paper are from preliminary test runs. The data served primarily to establish that the unit processes performed as expected. Comparisons between processes at this stage of the project can only be of a qualitative nature. Many more runs will be necessary for accurate evaluations of alternative treatment processes.

This experimental work is being conducted at the USEPA's Test and Evaluation (T&E) Facility in Cincinnati, Ohio, by the Treatment Technology Staff of the Alternative Technology Division, HWERL, ORD. This effort is contractor-supported by the University of Cincinnati, College of Engineering.

II. Experimental Approach

Unit Process Design

For the purposes of this work, the following unit processes are considered to be conventional technologies: lime precipitation, flocculation, clarification, and mixed media filtration. The advanced technologies are: sulfide precipitation, ion exchange and activated carbon adsorption. The conventional treatment technologies were given initial design consideration so that comparisions between the two groups of technologies would not be biased toward the advanced. The unit processes described here are only those which have been tested; other processes will be included as testing proceeds, or as the need to provide specific performance data arises.

One important feature of this project is the system's flexibility. Since it was not designed for one specific waste stream, it can be made to handle different types of "real world" electroplating and metal finishing wastes. The experimental treatment system can then be adapted to the various problems experienced by industry in treating their wastes.

An overall schematic of the experimental system is shown in Figure 1. A description of the design for each of the unit processes follows:

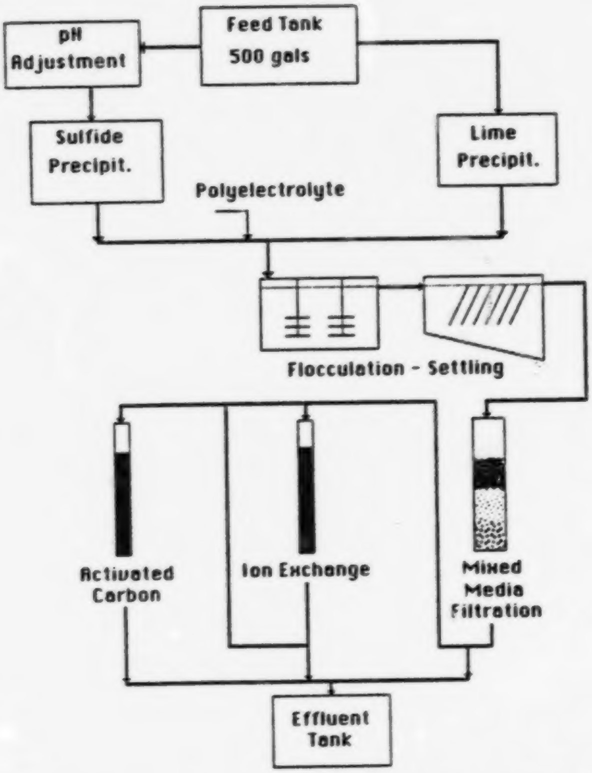
pH Adjustment
Feed Tank
500 gals
Sulfide Precipit.
Lime Precipit.
Polyelectrolyte
Flocculation - Settling
Activated Carbon
Ion Exchange
Mixed Media Filtration
Effluent Tank

Figure 1. Treatment System Schematic.

1) Lime Precipitation. Lime precipitation was selected as the primary conventional treatment technology because it is the most widely used process for the removal of heavy metals from electroplating wastewater. The main advantage of lime over other hydroxides is its low cost.

The two most important design considerations for the lime precipitation process are the retention time and the pH maintained in the reactor. The design mean residence time for the reactor is 33 minutes. A proportional pH controller was used to maintain a stable pH. Depending on the constituent metals in the waste stream, pH was maintained between 9.5 and 10.5. The contents of the reactor were well agitated to ensure uniform mixing of the lime slurry with the feed. A baffle was placed along the center of the cylindrical tank to avoid channeling. The pH control probe was placed in the first half of the reactor, while a second probe was placed near the overflow to compare the exit pH with that of the controller. The readings of the two pH probes were close enough to confirm that the controller probe was seeing the true pH which was maintained within ± 0.2 of the desired value.

2) Flocculation. The flocculation tank has a retention time of 60 minutes, based on a flow rate of 2.5 gpm. The tank's 147 gallon volume was divided into two compartments. Each compartment contained a slow-speed mixer to aid the flocculation process. A general-purpose anionic polyelectrolyte was added at a dosage of approximately 54 mg/l. Jar tests were conducted to optimize the dosage for each respective waste batch.

3) Clarification. A plate settler with inclined plates or lamelae was designed for the clarification step. On the basis of a 75 gal/d/ft^2 loading rate, a total of 48 ft^2 of plate surface area was required for a 2.5 gpm flow rate. Sixteen 2 ft. by 2 ft. plates were installed with an inclination of 75° to the horizontal. This produces a safety factor of 1.33 in the settling design. The retention time in the settling tank was 55 minutes. All 16 plates were connected to move as a unit, allowing the inclination to be changed from 60° to 90° to ensure that sludge did not accumulate on the plates. The tank bottom was inclined at a grading of 13:48 along its length to collect sludge at the drain. After each run, the sludge was drained into drums, and the tank was flushed.

4) Mixed Media Filtration. Mixed media filters were used to remove the fine suspended particles which did not settle in the clarification step. Two 12 inch plexiglass columns were available with one serving as a back-up. The media consisted of an 18 inch anthracite layer on top followed by a 15 inch sand layer which were supported by an 8 inch layer of gravel. The effective size of the anthracite particles was 1.2 mm with the sand being 0.45 mm. Running at 2.5 gpm, the filtration rate was 3.2 gpm/ft^2 (130 l/min · m^2).

5) Sulfide Precipitation. Sulfide precipitation using insoluble ferrous sulfide has been demonstrated to be an effective alternative to hydroxide precipitation for the removal of heavy metals from industrial wastewaters.[4]

To obtain best removal of metals, the pH must be adjusted to ~ 10.5 prior to the addition of ferrous sulfide. Lime was used for the pH adjustment. A 10% ferrous sulfide slurry was added to the waste stream in a small reactor following the pH adjustment at a rate of 36 ml/min (380 mg/l). The residence time of this reactor was 10 minutes. The flocculation aid was added to the waste stream immediately following the sulfide reactor.

6) Ion Exchange. Two six inch columns were utilized for ion exchange. Initially, one column was used for cation exchange and the other for anion exchange. Due to the volume limitations imposed by selecting a six inch column, only 0.5 ft^3 of resin could be loaded into the cation exchange column. This produced a service loading rate of 5 gpm/ft^3, which is the upper limit of the recommended range. After the second run, it was found that the loading rate was too high and that the resin would have to be regenerated too frequently. The second column was then loaded with another 0.5 ft^3 of cation resin. The columns were used in series. The cation exchange resin was a crosslinked macro reticular resin with a selectivity for heavy metal cations. The cation exchange capacity was 1.0 meq/ml of wet resin.

The cation exchange resin was regenerated using 5% HCl, followed by 4% NaOH in order to convert the resin to the sodium form. The resin was then rinsed with water to free the excess sodium hydroxide. Approximately 10 gallons of HCl was required per cubic foot of resin, 20 gallons of NaOH for neutralization and 75 gallons of water for rinsing.

7) Activated Carbon Adsorption. Activated carbon adsorption of heavy metals is a fairly new technology. There are a few reports showing limited success for the removal of individual metals using powdered activated carbon (PAC). Huang[5] tested column reactors using beads prepared from PAC using a special polymerization technique. There have been a few reports of using granular activated carbon (GAC) for the removal of low concentration heavy metals from municipal wastewater (wastewater spiked with up to 5 mg/L for each metal). GAC may be useful as a means of adsorbing degreasers and chelating agents from electroplating wastewater.

For this study, a 6 inch plexiglass column was used for the GAC adsorption process. The bed depth was 16 inches. Typical GAC of mesh size 4 x 10 was tested. The calculated loading rate of 12.5 gpm/ft^2 was above the recommended operating range of 2 to 10 gpm/ft^2. For future tests utilizing GAC, a greater bed depth and a lower loading rate will be used.

Waste Stream Descriptions and Handling

The source of the wastewater for these experiments was a local Cincinnati Metal Finisher who has been involved with joint EPA demonstration projects in the past. The metal finishing plant is a multi-process facility which incorporates both automatic and mechanical barrel, rack and hoist operations for zinc, brass, chromium, tin, bright nickel and cadmium plating. This plant operates a waste pre-treatment system that handles three segregated process streams:

1) Mixed acid/alkali metal rinse baths devoid of Cr^{+6} and CN (EPA RCRA codes D006/D008);

2) CN process streams and rinses. (EPA RCRA codes F007 and F009);

3) Cr^{+6} from chrome plating baths. (EPA RCRA code D007).

Although this research will ultimately treat wastes representative of each of these process streams, including the demonstration of difficult treatment challenges, the work described here deals with only the former. The metal finisher supplying the waste spiked the wastewater with drag-out to provide full-strength hazardous constituents, high enough in concentration to test the efficiency of the experimental treatment train. The wastes supplied for each run are further discussed in the results section.

The safe handling of these wastes was a matter of very serious consideration during the planning of this project. Every effort was made to keep within the bounds of the strictest interpretation of the regulations which apply. All the wastes brought into the T&E Facility were manifested out of the plater's facility and hauled by a licensed hazardous waste transporter. The wastes were transported in 55 gallon drums (typically, 8 to 10) that which had been leaktested prior to use. As soon as the drums were received, their contents were transfered to a 500 gallon polyethylene feed tank. The run effluents were contained in another 500 gallon polyethylene tank until it was verified that the effluents had been treated to the concentration levels acceptable for discharge to the Metropolitan Sewer District (MSD). All sludges have been retained for fixation/ stabilization studies where some may be sent for offsite characterization. The remaining sludge will be manifested to an authorized hauler/disposer for final disposition.

Sampling and Analysis

A sampling program was set up to collect the effluent from each of the unit processes utilized for that run. Sampling for each run began with the feed. Upon achievement of overflow in the clarifier, sampling was initiated. Sampling proceeded for each successive unit immediately following achievement of steadystate flow. All samples were taken manually from completely-filled pipes via permanent sample ports. Samples were placed in 500 ml polyethylene, screw-top bottles and acidified to below pH 2 with nitric acid. All analyses were performed at EPA's HWERL Lab, using EPA standard methods for atomic absorption spectrophotometry.

III. Results

At the time this paper was being prepared, four test runs had been completed. As each test run was slightly different from the others, they will be discussed separately.

Run 1

The waste received for the first run was dilute. The average concentrations of the feed induced into the treatment system are shown in Table 2.

TABLE 2

Metal	mg/l
Cadmium (Cd)	0.35
Chromium (Cr)	<0.50
Copper (Cu)	0.42
Iron (Fe)	9.1
Lead (Pb)	<0.50
Nickel (Ni)	11.4
Zinc (Zn)	8.7

The processes used for the treatment train were: lime precipitation (pH 9.5), un-aided flocculation, clarification, mixed media filtration, and activated carbon adsorption. After mixed media filtration, only Ni remained in the stream above the detection limit (for flame AA), at a concentration of 0.35 mg/l. Following the activated carbon column, Ni was below the detection limit. This first waste was successfully treated using conventional technologies. While it is doubtful this waste would even be classified as hazardous, the system did meet all performance expectations.

Run 2

In addition to the high metal concentrations shown in Table 3, the second waste contained degreasers and chelating agents absent in the first waste. Ammonia was evident by smell. Suspended solids were also seen in the feed tank. For the first 300 gallons of flow, the tank was not agitated; during the last 225 gallons, the solids were kept in suspension. The difference in the feed concentrations of the metals is clearly shown in Table 3.

TABLE 3. Process Effluent Results: Run 2.

		All Concentrations in mg/l						
		Cd	Cr	Cu	Fe	Ni	Pb	Zn
Feed a. quiescent	mean	149.7	17.4	25.0	9.3	127.3	<0.5	177.7
	st. dev.	13.2	0.6	2.7	0.4	11.7	0.0	2.2
b. agitated	mean	212.3	98.6	28.5	33.7	130.5	5.7	413.5
	st. dev.	41.9	19.4	5.5	6.6	24.9	0.6	63.3
	weighted average	176.5	52.2	26.5	19.8	128.7	2.7	278.8
Clarifier	mean	48.5	6.1	22.9	1.7	113.7	<0.5	45.8
	st. dev.	4.9	1.1	1.2	0.7	6.8		7.0
Mixed Media	mean	38.7	3.1	22.1	0.4	113.2	<0.5	23.0
	st. dev.	3.6	.3	1.2	.4	4.0		4.2
Ion Exchange*	mean	0.24	2.45	3.56	<0.3	22.5	<0.5	23.1
	st. dev.	0.19	0.27	3.08		11.86		0.75
Activated Carbon*	mean	35.7	2.7	17.9	0.1	116.8	<0.5	23.1
	st. dev.	1.3	0.1	2.1	0.2	2.5		2.4

* These processes were run alternately.

The unit processes chosen for this run were: lime precipitation (pH 9.5), un-aided flocculation, clarification, mixed media filtration, granular activated carbon adsorption and ion exchange. The first 100 gallons were run through the ion exchange columns, the remainder went through the activated carbon column.

The removals achieved by the various processes are shown in Table 4. The processes up to and including filtration successfuly removed Cr, Fe, Pb and Zn, (>80%) but could not precipitate or filter all the Cd, Cu, or Ni. It is thought that these elements were complexed with either ammonia or with some other component of the waste, preventing precipitation. The activated carbon column provided only a marginally better effluent. Since this same carbon was used for the first run, its sorptive capacity may have been reached. The ion exchange process removed substantial amounts of the metals coming through the mixed media filter. Figure 2 shows the ion exchange effluent concentration as a function of flow volume. Trend in the effluent concentration is an indication of the ion exchange resin approaching its capacity. The waste brought in for this run proved difficult to treat by conventional means. Since three-quarters of the waste had not gone through ion exchange, the metal concentrations in the effluent were still very high, as evidenced by the deep-blue color. It was decided to perform another run to further treat this effluent.

TABLE 4. Cummulative Removal Efficiencies: Run 2

Effluents	Cummulative % Removed Cd	Cr	Cu	Fe	Ni	Pb	Zn
Clarifier	73	88	14	91	12	82	84
Mixed Media	78	94	17	98	12	82	92
Activated Carbon*	80	95	32	99	9	82	92
Ion Exchange*	99.8	95.3	86.6	98.5	82.5	82	99.8

* These processes were run alternately.

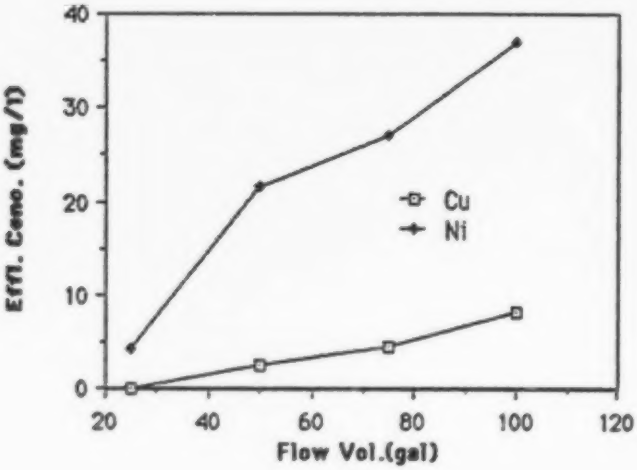

Figure 2. Ion Exchange Effluent -vs- Flow Volume

Run 2A

Since this effluent had already been treated by lime precipitation (at pH 9.5), it was decided to add both ferrous sulfide precipitation and enhanced flocculation sulfide and an anionic coagulation aid to the treatment train. The ferrous sulfide was added as a 10% slurry at approximately 36 ml/min (380 mg/L) directly following lime precipitation at pH 10.5. The coagulation aid was diluted approximately 250 times and added at a rate of 85 ml/min (54 mg/L) at the head of the flocculation tank. After clarification and filtration, the flow passed through the ion exchange column. The resin was not regenerated since only 100 gallons had been put through during the previous run and it was believed to still have additional capacity.

The results of this run are shown in Table 5 with the calculated removals shown in Table 6. The feed concentrations for this run were slightly higher than the effluent from the previous run due to the mixing of approximately 40 gallons of untreated waste and various tank wash-outs with the effluent. Although direct comparison is difficult, it does appear as if the treatment train, up to and including the mixed media filter, was more effective than the one used in the previous run. Only Cr and Fe were removed to a lesser degree, while removals of the other elements were substantially increased. This may be partially explained by the fact that the feed concentrations for this run were lower. The decrease in Cr removal may have also been caused by the pH increase from 9.5 to 10.5 between the two runs. Chromium becomes more soluble as pH increases above 8. The change in removal of Fe may have been an interference caused by the ferrous sulfide.

TABLE 5. Process Effluent Results: Run 2A

		All Concentrations in mg/l						
		Cd	Cr	Cu	Fe	Ni	Pb	Zn
Feed	mean	28.6	7.2	11.1	4.3	76.9	<0.5	36.3
	st. dev.	1.2	.3	0.0	0.2	1.4	0.0	1.4
Clarifer	mean	4.9	1.6	8.8	0.3	54.5	<0.5	3.7
	st. dev.	1.2	.2	1.9	0.1	7.1		0.8
Mixed Media	mean	3.1	1.1	8.2	<0.3	53.5	<0.5	1.2
	st. dev.	2.3	0.1	2.9		12.7		0.5
Ion Exchange	mean	0.5	1.1	5.2	<0.3	28.7	<0.5	3.9
	st. dev.	0.1	0.1	1.4		8.1		2.1

TABLE 6. Cummulative Removal Efficiencies: Run 2A

	Cummulative % Removed					
Effluents	Cd	Cr	Cu	Fe	Ni	Zn
Clarifier	83	77	21	92	29	90
Mixed Media	89	84	26	93	30	92
Ion Exchange	98.1	84.8	53.5	93.1	62.7	89.1

The ion exchange column had reached its capacity for Ni and was close to its capacity for Cu. The effluent concentrations for this run were too high to permit disposal. After the run, the ion exchange column was regenerated and the entire run's effluent was passed back through without additional treatment. Analyses of this effluent for Ni, the most troublesome of the elements in this waste, showed concentrations of 13 to 18 mg/l, respectively.

Run 3

The plan for the third run was to obtain a waste similar to that of Run 2 and test a treatment train similar to that used in Run 2A. Thus, the treatment train consisted of: pH adjustment (pH 10.5), sulfide precipitation, polymeraided flocculation, clarification, mixed media filtration and lastly, ion exchange. For this run, an additional ion exchange column with a slightly greater bed depth was used in series with the original column to more than double the capacity. The dosages of ferrous sulfide and the flocculation aid were the same as those used in Run 2A. The results are presented in Table 7 and 8.

TABLE 7. Process Effluent Results: Run 3.

		All Concentrations in mg/l						
		Cd	Cr	Cu	Fe	Ni	Pb	Zn
Feed	mean	194.6	60.1	29.0	17.4	98.6	22.2	415.
	st. dev.	35.6	18.2	0.9	7.8	3.7	13.3	94
Clarifier	mean	26.4	3.2	20.0	0.6	85.3	<0.5	31.1
	st. dev.	5.8	0.7	1.6	0.2	2.0		9.2
Mixed Media	mean	24.3	2.1	22.7	<0.3	85.3	<0.5	30.9
	st. dev.	4.1	0.2	1.6		2.0		4.6
Ion Exchange	mean	0.4	1.4	2.3	<0.3	13.4	<0.5	0.4
	st. dev.	0.1	0.1	2.4		8.7		0.5

TABLE 8. Cummulative Removal Efficiencies: Run 3

Effluents	Cd	Cr	Cu	Fe	Ni	Pb	Zn
	Cummulative % Removed						
Clarifier	86	95	31	97	14	98	93
Mixed Media	87	96	22	98	14	100	93
Ion Exchange	99.8	97.7	92.0	100.0	86.5	100.0	99.9

The Run 3 waste was indeed very similar to the Run 2 waste. The concentration of Pb in Run 3 was higher, while the Ni concentration was slightly lower. The concentrations of the other metals were practically the same. The data show that the processes in this treatment train, up to and including mixed media filtration, were able to substantially remove Cr, Fe, Pb and Zn (>90% cummulative removal), but were not able to provide the same order of treatment for Cu and Ni. The added ion exchange capacity proved to be adequate for the treatment of the entire waste stream volume. Comparative results between lime and sulfide precipitation are shown below in Figure 3.

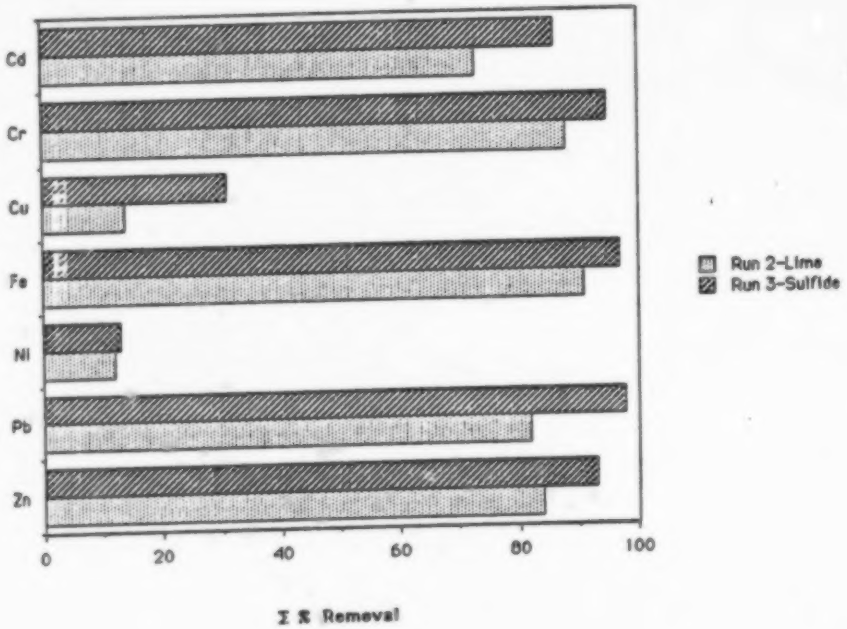

Figure 3. Clarifier Removal Efficiency: Lime vs. Sulfide Precipitation

IV. Conclusions

1) A versatile treatment system for aqueous hazardous metals wastes has been established at the USEPA's Test & Evaluation Facility.

2) The preliminary performance data has shown to be consistent with standard treatment practices.

3) Sulfide precipitation exhibited greater metals removal potential over lime precipitation.

4) Complexed nickel proved to be more difficult to treat even after advanced treatment techniques of ion-exchange and activated carbon adsorption.

V. Future Work

Projected research efforts will include:

1. The evaluation of techniques to be used for removal of interferences (e.g. complexed nickel, organics, etc.) encountered during the first phase of the treatability studies presented herein;
2. Treatability of aqueous cyanide-metal bearing hazardous wastes with RCRA codes F007 and F009 will be demonstrated. This will include assessment of techniques currently employed for cyanide destruction (e.g. alkaline chlorination) as well as more advanced techniques (e.g. ozonation) and
3. Sludge characterization studies will also be conducted which will compare state-of-the-art stabilization/fixation techniques. TCLP's will be performed to assess the leaching potential of metal treatment sludges (RCRA codes F006 and F008).

VI. References

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3. Ibid.

4. Peters, R.W., Y Ku, and D. Bhattacharyya, "Evaluation of Recent Treatment Techniques for Removal of Heavy Metals from Industrial Wastewaters.", AIChE Symposium Series, 81 (243), 165-203, 1985.

5. Huang, C.P., "Activated Carbon Process for the Treatment of Cadmium (II) - Containing Wastewaters", EPA-600/S2-83-061, 1983.

WHY NOT SIMPLIFY WASTEWATER COMPLIANCE?

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Not long ago metal finishers, battery manufacturers, iron and steel producers and others in the metals industry were required to do nothing more than neutralize acidic wastewaters before releasing them to the local sewer system. These discharged waters, however, still contained significant concentrations of toxic metals like lead, copper, chromium, zinc, nickel and cadmium which are harmful to human and aquatic life. Growing environmental concern prompted legislation like the Clean Water Act, which imposes rigorous restrictions on the amount of contaminants left in discharged waters. This Act requires industry to not only neutralize wastewaters but to remove toxic heavy metals from their wastewaters.

Many manufacturers have had trouble complying with these governmental standards because removing heavy metal contaminants from wastewater is not always easy or even possible using conventional methods. Imagine a new technology that can treat water containing toxic heavy metals and leave it clean enough to pass the Environmental Protection Agency's primary drinking water standards! Imagine that this same technology will retrofit easily into your existing wastewater treatment facility. Such a technology does exist, and it is revolutionizing the performance of conventional wastewater treatment facilities. This new process technology does not rely on thermodynamic solubility laws for metal removal. Instead, it uses a unique coprecipitation-encapsulation technology to link the solubility of toxic metals to that of iron. The kinetically driven process then encapsulates heavy metals in a very stable, highly insoluble iron matrix.

A New Technology

UNIPURE^{SM} Process Technology was developed by Unocal's Science and Technology Division in the early 1980's. The goal was to use common chemicals and hardware to achieve uncommon results. Initial research was directed toward the metal industry's most highly contaminated wastes such as spent pickle liquors and other plating and processing baths. Recognizing that these wastes are highly enriched with chemical components it was felt that it might be possible to put these wasted resources to work, so as to, in effect, have the wastewater treat itself.

Half the battle is recognizing that process technology and not hardware is the limiting factor in conventional wastewater treatment. What remained was to specifically develop a new process technology that could conveniently be applied in existing wastewater treatment facilities.

Traditional Strategies

It might be helpful to first examine how a conventional wastewater treatment facility works. This, along with a description of conventional process technology, will provide a basis for understanding why this new process technology was developed. Most wastewater is highly acidic and contains a variety of soluble heavy metals. The most common strategy utilized in treating wastewaters invokes the following process steps; waste segregation/collection, metals precipitation, and effluent clarification.

Wastewaters from various manufacturing processes are sometimes segretated and pre-treated (eigher physically or chemically) as necessary. Oil removal, filtration, chromate reduction, and cyanide oxidation are common examples of pre-treatment. After pre-treatment, the wastewaters are collected and sent to the Neutralization Tank. Here, a base such as lime or caustic soda is added to raise the pH, thus increasing the hydroxide ion concetration. This causes toxic heavy metals to precipitate. The resulting solid liquid suspension is flocculated and then clarified. In many cases filtration is necessary to remove suspended solids not collected during clarification. Collected solids off the bottom of the clarifier are further dewatered using a filterpress, vacuum drum filter, or other similar device. The dewatered solids are then hauled to and disposed of in the appropriate waste disposal site.

Traditional Chemistry

In all conventional alkaline precipitation wastewater treatment facilities, the purpose of the neutralization step is to sufficiently raise the pH so that toxic heavy metals become insoluble and precipitate from solution. That is, toxic heavy metals react with the hydroxide present to form insoluble metal hydroxides. In general, these insoluble metal hydroxides form according to the following reaction:

$$\text{Reaction 1.)} \quad M^{++} + 2OH^{-} \rightleftharpoons M(OH)_2$$

The extent to which the soluble metal is converted to an insoluble hydroxide is governed by the laws of thermodynamics. It is common belief that the more hydroxide present, the more complete metals precipitation. To a certain extent this is true, but too high a pH can actually resolubilize precipitated metal hydroxides according to the following reaction:

Reaction 2.) $M(OH)_2 + OH^- \rightleftharpoons M(OH)_3^-$

In reality there is an optimum pH for maximum metal removal. This optimum pH is different for every metal and varies according to the thermodynamic solubility properties of the metal (see Figure 1).

It is important to note that this optimum removal limit is described by thermodynamics. Increasing or decreasing the pH from this point will solubilize the metal and decrease its removal. When several different metals must be removed, the pH is adjusted to reflect the best overall performance; a compromise situation since optimum removal of every metal is not possible.

Thus, with conventional alkaline precipitation, treatability or metals' removal will always be a compromise and even under the most optimal conditions cannot be expected to exceed the value predicted by thermodynamics. In reality, many other factors can further compromise treatability. Some of these factors, such as chelating agents, affect the actual metal precipitation process. Still others affect the removal of the precipitated solids from solution such as the formation of colloids or gelatinous low density solids. However, these constraints are not generic to the wastewater treatment facility, but rather the result of the process technology being employed. For example, the effect of chelating agents on treatability increases with pH. They exert their greatest influence at the high pH required for alkaline precipitation. Finely divided colloidal solids and slow settling gelatinous precipitates result from the high surface charge imposed upon solids formed in a highly alkaline environment. Thus, these often observed treatment "limitations" or problems are simply symptoms of the process technology employed.

In addition to alkaline precipitation, other thermodynamic precipitation technologies such as sulfide precipitation, and carbonate precipitation operate under the constraints described above. That is they all have (1) thermodynamically defined limits for metal removal and (2) to one extent or another display many of the problems associated with conventional alkaline precipitation.

Thermodynamic processes are driven by kinetics. For example, Reaction 1.) shows both a forward (left to right) and reverse reaction (right to left). When the rate of the forward reaction equals the rate of the reverse reaction, thermodynamic equilibrium is achieved and you have arrived at a point described by the curves in Figure 1. If your objective was to precipitate soluble heavy metals, you would ideally prefer that only the forward reaction take place. However, reaction thermodynamics dictate that as long as the newly developed solid is exposed to the solution, the reverse reaction must also take place. This acts against your primary objective. Wouldn't it be nice if, in effect, you could remove the newly precipitated metal hydroxide solid from the solution environment as quickly as it forms. This "kinetic" mechanism would eliminate the reverse reaction and allow unlimited metals removal. In essence this is exactly what Unocal's iron coprecipitation-encapsulation process technology accomplishes. Activated iron is used to attach and bind soluble heavy metals, then as the highly insoluble iron is precipitated from solution it carries or coprecipitates the heavy metals. Specially designed process conditions then encapsulate the coprecipitated heavy metals in a highly stable iron matrix thus removing the coprecipitated metals from the environment of the solution.

UNIPURE Process Technology

UNIPURE Process Technology centers around the solubility of a single element, iron, rather than around the individual solubilities of the various toxic heavy metals. The UNIPURE Process is designed to activate the iron innate to the wastewater (additional iron can be added if necessary). Unocal scientists discovered that when properly activated, iron was capable of binding soluble toxic heavy metals. They then developed a method for bringing the iron out of solution, with the heavy metals still bound to it, in such a way as to encapsulate the metals and isolate them from the solution.

Metals removal efficiency is directly related to the conditions under which this process is implemented. The most crucial requirements are designed into a unique reactor system to insure consistent efficacy. During treatment, heavy metals become locked within a stable iron matrix (see Figure 2) which forms a dense, highly flocculated solid. This solid can easily be separated from solution using conventional clarification and filtration techniques. Other than iron, no additional treatment chemicals are required. The UNIPURE Reactor system can be substituted for the traditional Neutralization Tank and allows a simple retrofit into an existing wastewater treatment facility (see Figure 3).

A Flexible Technology

The extraordinary flexibility of this new technology permits a free choice of neutralizing base (including ammonia). By tying process control to the chemistry of a single, highly insoluble metal, iron, rather than the various metals being treated, pH control requirements are greatly eased. Simply maintaining treatment conditions in excess of pH neutrality is usually sufficient.

The flexibility of this new metals removal process eliminates the need for segregated pre-treatment of difficult to treat waste streams such as those containing hexavalent chrome, complexing agents, etc. Only highly oily streams, or those containing cyanide, need to be segregated and pretreated. Since the process is carried out at a lower pH than conventional treatment, colloids and gelatinous solids can be avoided, the resulting sludge contains less water, and this reduces sludge disposal costs. In addition, heavy metals are locked within a very stable iron matrix. This chemical stability immobilizes the heavy metals and makes them significantly less susceptible to leaching by acids. The iron matrix itself is soluble to no more than 3 to 4 parts per billion at pH 4.5.

Highly Effective

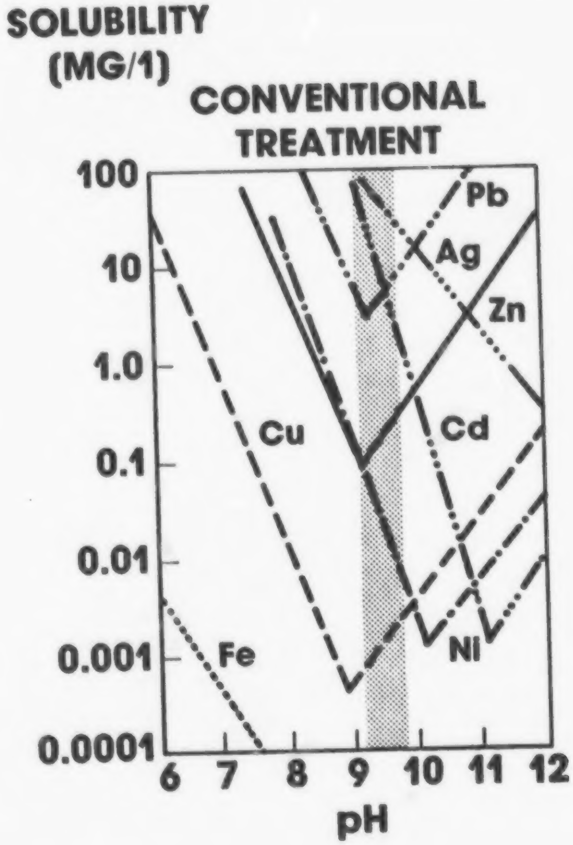
Unocal's new iron coprecipitation-encapsulation process has been proven in bench-scale laboratory testing, automated pilot units, and actual commercial application. This technology was first commercialized in early 1983. Today discharges from the job shop electroplating, aerospace fastening, metal galvanizing, battery manufacturing and iron and steel industries are enjoying the many benefits of this innovative technology.

Table 1

UNIPURE EFFICACY DATA

INDUSTRY		Untreated	UNIPURE
Battery:	Cu	0.1	0.05
	Pb	3.0	0.02
	Zn	0.4	0.07
Galvanizing:	Cr VI	2.9	0.1
	Zn	58	0.2
Iron & Steel:	Cr	10.5	0.03
	Pb	1.4	<0.05
	Zn	30.4	0.1
Metal Finishing:	Cd	18	0.1
	Cu	12	<0.01
	Ni	0.9	<0.05
	Pb	0.1	<0.05
	Zn	82	0.08

THEORETICAL SOLUBILITIES OF METAL HYDROXIDES AS A FUNCTION OF pH



SOURCE: EPA DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS FOR THE METAL FINISHING POINT SOURCE CATEGORY

FIGURE 1.

INSOLUBLE ACTIVATED – IRON MATRIX FORMATION

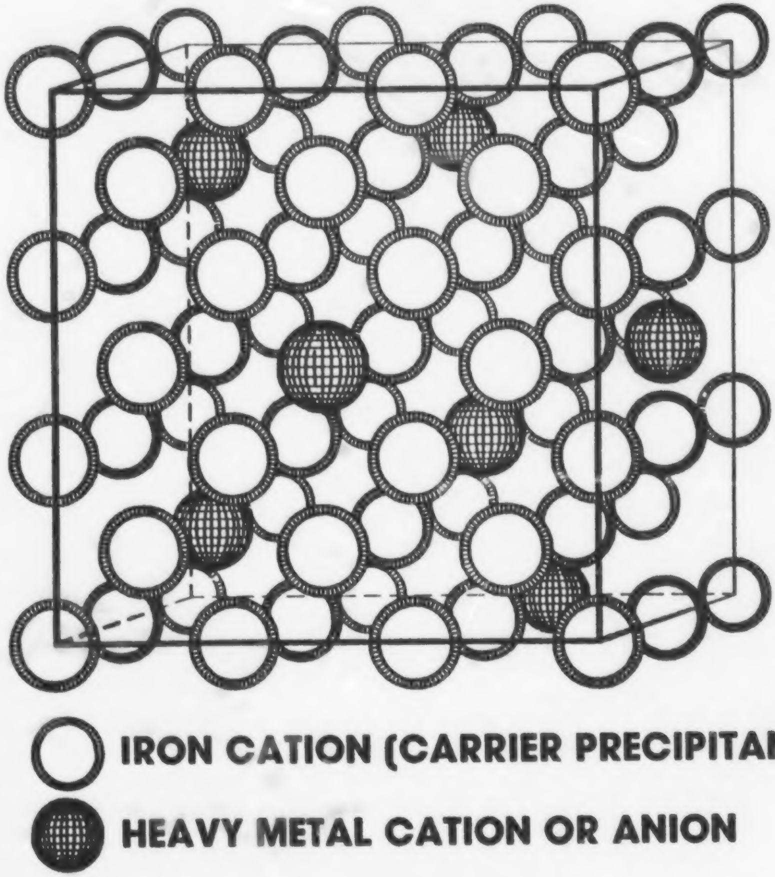

○ IRON CATION (CARRIER PRECIPITANT)
● HEAVY METAL CATION OR ANION

FIGURE 2.

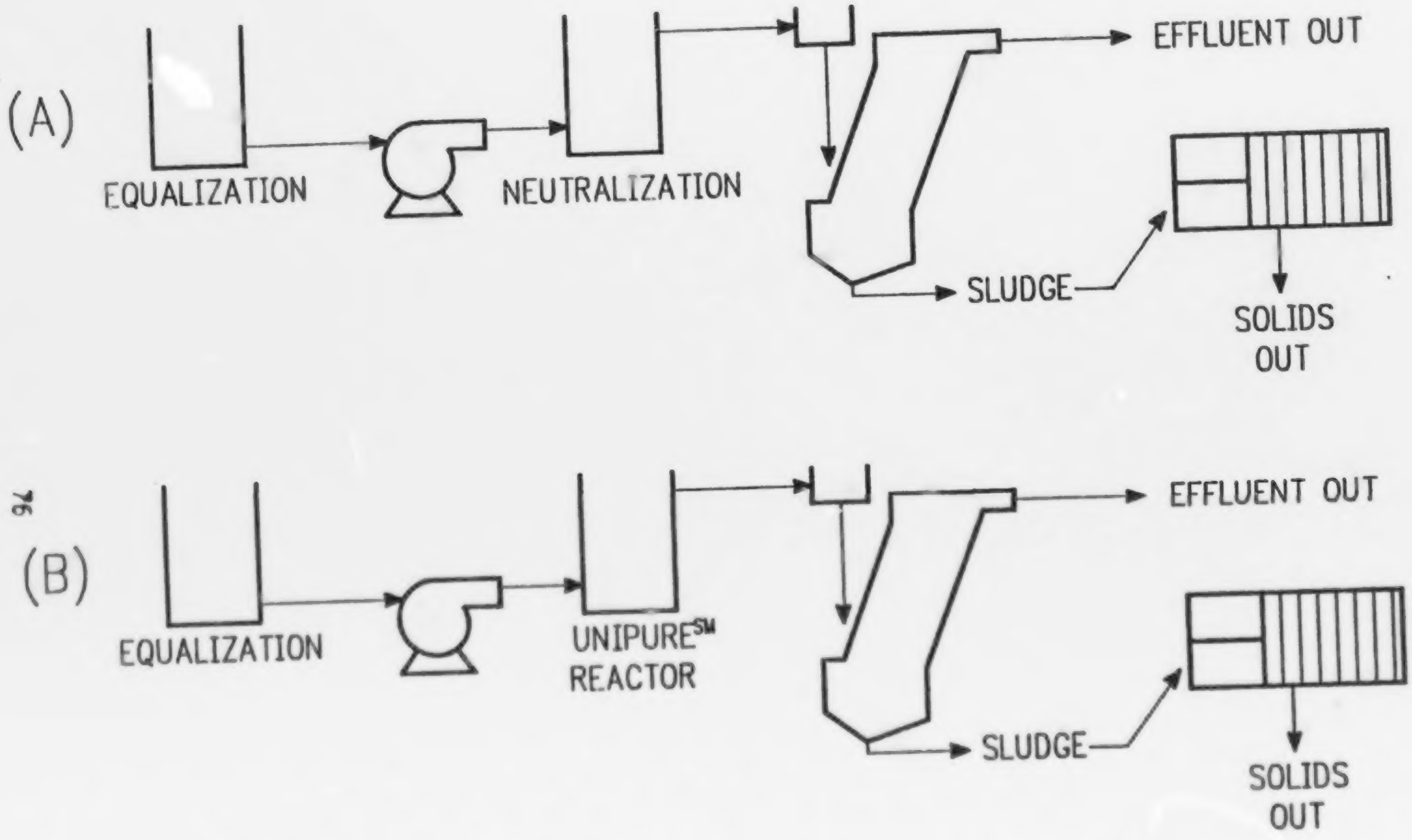

(A)
EQUALIZATION
NEUTRALIZATION
EFFLUENT OUT
SLUDGE
SOLIDS OUT
(B)
EQUALIZATION
UNIPURE^SM REACTOR
EFFLUENT OUT
SLUDGE
SOLIDS OUT

FIGURE 3: SCHEMATIC (A) SHOWS A CONVENTIONAL TREATMENT SCHEME AND SCHEMATIC (B) SHOWS THE UNIPURE RETROFIT

FIGURE 3.

LIABILITY FOR MANAGING HAZARDOUS WASTES: PAST, PRESENT AND FUTURE

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I. Introduction.

This paper examines the current legal framework applicable to the handling of hazardous substances and wastes. It focuses on the complex regulatory program governing hazardous wastes now being generated and the theories of liability available to address improper past disposal practices.

For years industry has been developing advanced technologies and manufacturing processes creating a multitude of new consumer products. From sophisticated electronics and appliances to newly discovered coatings for consumer goods, we reap the benefits of our ever-expanding industrialization. Unfortunately, this rapid development does not come without a price. The waste materials generated along with these products, at least from a historical perspective, were managed (or mismanaged) with little regard for long term, environmental impacts. It was not until the discovery of waste disposal horrors across the country, that the "throwaway mindset" of the 50's and 60's gave way to the new environmental awareness of the 80's; the realization that wastes must be treated and disposed of only after careful planning and forethought. The cost to industry of its past waste disposal practices and the rigorous standards that must be met now are extraordinary, and the legal liabilities are limitless.

II. Federal Regulatory Scheme.

A. General Environmental Legislation

The comprehensive environmental legislative package crafted by Congress in the 1970's deals with every aspect of environmental control. All major environmental programs administered by the federal government were addressed in that decade.

1. The Clean Air Act of 1970, as amended,[1] requires industry, after an initial planning period by the states, to control emissions of certain designated air pollutants resulting in the installation of expensive, energy intensive air pollution control equipment. It also requires the control of certain toxic air pollutants.

2. The Clean Water Act of 1972, as amended,[2] requires the federal government to establish effluent criteria for categories of industry and compels industry to obtain permits for each point source discharge of pollutants to navigable waters. The levels of technology industry must install become increasingly more stringent over time, making necessary periodic investments in water pollution control equipment. The Clean Water Act also establishes the framework for a pretreatment program for discharges to public sewer systems applicable to many electroplaters and surface finishers.

3. The Safe Drinking Water Act of 1974,[3] resulted in the establishment of maximum contaminant levels permitted to remain in drinking water supplied for public consumption.

4. The Toxic Substances Control Act of 1976,[4] regulates the introduction into commerce of new chemical substances and the testing of certain existing chemical substances to determine their potential environmental impact when distributed in commerce. It also provides the requisite authority for a comprehensive regulatory program dealing with the disposition of polychlorinated biphenyls ("PCBs").

The final piece of major environmental legislation enacted during this period was the Resource Conservation and Recovery Act of 1976, as amended, ("RCRA")[5] which, in a sense, was Congress' effort to deal with environmental hazards not covered by the other statutes. The other laws deal with air pollution, water pollution, toxic chemicals in commerce, PCBs, and drinking water supplies. RCRA deals with the residues collected in pollution control equipment in addition to many other waste streams generated by traditional manufacturing processes.

B. The Hazardous Waste Program

Through the regulatory program mandated by RCRA, anyone involved with handling hazardous waste was required to register with the Environmental Protection Agency ("EPA") by August, 1980, indicating whether they generate, transport, treat, store or dispose of hazardous wastes. That initial notification was followed by a second submission to EPA in November, 1980, only by those facilities engaged in the treatment, storage or disposal of hazardous wastes.[6] These notifications were intended to provide EPA with a snapshot of the universe of participants handling hazardous wastes including the identification of the types of hazardous wastes each was handling and was a mandatory prerequisite for such activities to continue. Having obtained this information, EPA could then set about the task of issuing permits where necessary and inspecting facilities subject to regulatory obligations. With all entities handling hazardous waste now "within the system" and fully accountable, it was believed that the era of indiscriminate disposal of hazardous wastes would end.

Briefly, the general requirements of EPA's RCRA regulations[7] are as follows:

> 1. All facilities had to determine if any of the wastes they generated, transported, treated, stored or disposed of met the definition of "hazardous waste."[8] In many instances this was a difficult task due to the wide variety of industrial processes that had to be evaluated and the complexity of EPA's regulations defining hazardous wastes. Complicating the process further were the exemptions from the definition of "hazardous waste" carved out by EPA such as wastes which are otherwise hazardous but are not regulated because they are being recycled.
>
> 2. Once it was determined that hazardous wastes were being handled at a particular facility, the next step was to categorize the facility as a generator, transporter, storer, treator or disposer of these wastes. Again, the complex definitions of each of these terms led to subtantial confusion in the early stages of the regulatory program.
>
> 3. After determining that hazardous wastes were handled and properly classifying the facility, specific regulatory standards have to be met.
>
> > (a) Generators of hazardous waste have to obtain an identification number from EPA, properly package, label, mark and placard containers of hazardous wastes, and use a manifest when the hazardous wastes are

shipped off-site.[9] (A more limited set of regulations apply to "small quantity generators.") A generator is also precluded for storing hazardous waste for more than 90 days without qualifying to operate as a hazardous waste storage facility.

(b) Transporters of hazardous wastes have to obtain an identification number and comply with substantial recordkeeping requirements including the use of the manifest.[10]

(c) Facilities that treat, store or dispose of hazardous wastes ("TSDFs") are required to meet a rigid set of standards until they obtain a permit from EPA including waste analysis plans, training requirements, contingency plans, recordkeeping, periodic reporting, financial responsibility for closure and post-closure care, and the use of a manifest for receiving shipments of hazardous wastes.[11] Analagous, but often more stringent standards are specified for permitted facilities.[12]

In 1984, Congress amended RCRA adding significant new requirements. Rigid deadlines were placed on EPA for the issuance of permits to TSDFs.[13] Substantial limitations were imposed on the use of land disposal facilities (e.g. landfills) for certain hazardous wastes.[14] In addition, within RCRA Congress established a corrective action program similar to the clean-up requirements of the Comprehensive Environmental Response, Compensation and Liability Act, as both an enforcement option before a permit is issued,[15] and as a mandatory condition in all hazardous waste permits for TSDFs.[16] This corrective action program will place a substantial financial burden on any facility that needs a permit under RCRA, since it allows EPA to require the clean-up of any "solid waste management unit" located at the facility whether or not that unit ever handled hazardous wastes. The legislative theory behind the corrective action requirement is the notion that EPA should not issue RCRA permits to TSDFs that have on-site contamination problems from any source.

Significant enforcement authority is also vested in EPA and the public under RCRA. Administrative orders, civil penalties of up to $25,000 per day and a vast array of criminal penalties are available to redress violations of RCRA.[17] Of equal importance is the authority of citizens to enforce RCRA, including the imminent and substantial endangerment provision.[18]

Given this general overview of the RCRA hazardous waste regulatory program that, for the most part, applies prospectively (since 1980), industry has received a clear mandate as to their obligations with respect to hazardous wastes now being generated. Hazardous waste must be managed with the same care and concern as products. Under RCRA, industry must control hazardous waste activities and reduce the quantity and toxicity of the wastes generated.[19] There are significant regulatory and statutory liabilities imposed for non-compliance which are actionable by the government and third parties, drawing close parallels to the well-established principles of product liability. It may not be enough to rely on the periodic inspection by government representatives to assure compliance is being met. Instead, a comprehensive self-policing program is mandated.

III. Superfund - Responsibility for Disposal Practices.

Liability for the disposal of hazardous wastes both historically and in the future is also governed by the Comprehensive Environmental Response, Compensation and Liability Act, as amended by the Superfund Amendments and Reauthorization Act ("Superfund").[20] Under this imposing statutory scheme, which has been held to apply retroactively,[21] industry is saddled with the financial obligation to clean-up disposal sites where there is a release or threat of a release of hazardous substances that may endanger public health or the environment.[22]

This environmental legislation is as far-reaching as has ever been enacted. The standard of liability is strict and joint and several, meaning that there is no need for the government to prove fault, and any one liable party can be responsible for the entire clean-up.[23] Liability under Superfund flows merely from one's status not because of negligence or fault. Congress intended to develop a rigid all-encompassing clean-up program and, to accomplish that result, abandoned more traditional legal approaches.

Superfund establishes a hazardous substance response trust fund by imposing certain new taxes to enable the federal government to finance the clean-up of priority sites.[24] It also provides the mechanism for identifying these sites on a National Priorities List included as part of the National Contingency Plan ("NCP").[25] The NCP establishes the procedures for investigating, evaluating and remedying environmental problems at the priority sites and sets forth the procedures to be followed by EPA in seeking participation by responsible parties. With these broad procedures and authority, it is important to understand that Superfund applies to releases or threatened release of "hazardous substances,"[26] a term far broader than the "hazardous wastes" regulated under RCRA. In fact, a "hazardous waste" is merely a subset of the types of materials covered by Superfund.

Liability under Superfund is imposed on owners and operators of sites that require clean-up, owners and operators of these sites at the time hazardous substances were disposed of, generators of the substances, and transporters under certain circumstances.[27] There is no legislative or judicial guidance to aid in establishing priorities among the liable parties which has made allocation schemes difficult to develop.

EPA is authorized to undertake removal actions at any site, however these clean-ups are limited to expenditures of less than $2,000,000 over a one year period.[28] Remedial actions can be taken only at NPL sites and are not limited in time or money.[29] Generally, the NCP requires EPA to conduct a Remedial Investigation to identify the environmental problems at a site and a Feasibility Study to evaluate available remedies. EPA's clean-up remedy must be "cost effective" taking into account the amount of money in the fund.[30]

After the studies are completed, normally at a cost well in excess of $500,000, EPA prepares a Record of Decision selecting the remedy. Public comment on the remedy is solicited before it becomes the final decision of EPA. Once this stage is reached and in many cases earlier, potentially responsible parties ("PRPs") considered liable by EPA have the opportunity to undertake the clean-up. These negotiations between PRPs and EPA are unique since unlike negotiations under other federal environmental programs, EPA can perform the clean-up itself and merely sue to recover its response costs. Obviously, the dynamics of this process make it difficult for PRPs to reach a satisfactory resolution, since it is difficult enough for the PRPs to even agree among themselves.

Recent Superfund amendments changed the complexion of the program. Congress required EPA to establish clean-up standards,[31] setting out legislative preferences and taking away some of EPA's discretion to determine "how clean is clean" on a case-by-case basis. The statute now sanctions buy-outs for de minimis contributors[32] and allows EPA to develop cost allocation schemes instead of forcing PRPs to do it among themselves.[33] One encouraging provision of the new amendments is the defense now available for "innocent purchasers" of sites ultimately determined to require clean-up under Superfund.[34]

It is certain that Superfund, particularly the new amendments, will undergo significant court review. Unfortunately, Congress limited the availability of judicial review by preserving prior judicial precedent precluding review of EPA's early decisions on remedies, and new cost allocation and de minimis buy outs, until EPA brings a cost recovery or other action.[35] (There also may be a way to raise these issues under the new citizen suit provision of Superfund.) As a result of these provisions together with the legislative direction for EPA to vigorously implement the Superfund program, industry appears to hold even fewer cards under the law.

IV. Controlling Future Liabilities.

A. Past Disposal Practices

There are lessons to be learned from the liability standards established in Superfund and the RCRA regulations applicable today that can serve as a guide for minimizing liability at sites previously used. Steps that can be taken to limit liability in the future from wastes generated in the past include the following:

> 1. Inventory past waste disposal practices and identify possible future Superfund sites before they are discovered by the government or other third parties. (You may have already identified such sites by complying with the reporting requirements of Superfund.[36]) Collect and evaluate all available records, considering current precedents established under Superfund. It is important to gain from current and former employees as much information as possible about past practices because company records usually prove to be inadequate.
>
> 2. Determine the current status of the sites that were used in the past based on the standards the government will consider in assessing the site

today. To do this, a great deal of information may be obtained from government files through the Freedom of Information Act[37] and comparable state laws.

3. Conduct the evaluation in a thorough and professional manner only after deciding that if the results are negative, they will be reported to the government. Failure to make this fundamental decision at the outset may create potential criminal liability for having information and not reporting it as may be required.

4. If necessary, especially if there are disposal areas on your own property, develop an appropriate remedy and assess potential claims against other parties who may also have contributed wastes to the site. Superfund allows for contribution claims for response costs and this opportunity to obtain additional funds should not be overlooked.[38]

5. If a clean-up is required, prepare the plan with the concurrence of the government. Since the government will inevitably learn of the problem, take the initiative to raise it first, together with your proposed clean-up program. This approach will serve to cut off any unilateral action by the government and will put you in the strongest negotiating position. It may also enable you to preempt any action by third parties who may seek to compel clean-up of the site.

These suggestions are aimed at enabling a company to minimize liability for past disposal practices by acting promptly, taking the initiative, and controlling costs. To the extent the government has not targeted the site involved, by adopting a pro-active approach, you are more likely to avoid the full impact of the rigors of Superfund. While a somewhat progressive view, it is realistic, logical and likely to save significant expense.

B. Present and Future Disposal Practices

The RCRA regulatory program is designed to address up front the unbounded liabilities imposed under Superfund, and, at the same time, to make Superfund cases easier for the government. Under RCRA, accurate records will exist by virtue of the manifest system and periodic reports that will enable the government to identify potentialy responsible parties. Even so, all is not lost.

When arranging for the disposal of hazardous wastes today, be sure you know who you are dealing with and what they are doing with the waste. Audit the TSDF to assure that the operator is complying with all applicable requirements. (You should really make sure the facility is complying with sound environmental practices which will often exceed the regulatory requirements.) Do not merely give your waste to the lowest bidder. Remember, any problem at the disposer's site may cost the generator.

Negotiate favorable contractual terms with the disposer. Will he indemnify you for any liability? Will he agree to be responsible to the government or third parties in the event of a claim? Raise your liability concerns, as you would with any other business concern, and attempt to negotiate adequate protections. Even if favorable contract conditions increase the price, the result may be worth it.

In addition to concerns over liability for off-site disposal, your own compliance status is also critical. Do your employees know how to handle hazardous wastes? (Has the required RCRA training been effective?) Are wastes being discarded unlawfully, for example, by dumping them down the sewer or "out back?" Can you account for all the wastes generated? Each of these concerns also need to be addressed in the day-to-day business setting just as you address concerns about your products.

Perhaps with the conscientious implementation of the RCRA regulatory program, there will be a time when Superfund will no longer be needed and wastes that are currently being generated and disposed of will all be handled properly. Until that time, however, industry can expect substantial financial burdens both in complying with current RCRA regulations and in addressing under Superfund the clean-up of sites used in the past.

FOOTNOTES

1. 42 U.S.C. §7401, _et_ _seq_.

2. 33 U.S.C. §1251, _et_ _seq_.

3. 42 U.S.C. §300f, _et_ _seq_.

4. 15 U.S.C. §2601, _et_ _seq_.

5. 42 U.S.C. §6901, _et_ _seq_.

6. 42 U.S.C. §6925

7. While this summarizes the federal regulatory program, the intent of RCRA is that the states adopt equivalent regulations and implement the hazardous waste program in lieu of EPA. 42 U.S.C. §6926

8. 40 C.F.R. Part 261

9. 40 C.F.R. Part 262

10. 40 C.F.R. Part 263

11. 40 C.F.R. Part 265

12. 40 C.F.R. Part 264

13. 42 U.S.C. §6925

14. 42 U.S.C. §6924

15. 42 U.S.C. §6928(h)

16. 42 U.S.C. §§6924(u) and (v)

17. 42 U.S.C. §6928

18. 42 U.S.C. §6972

19. 42 U.S.C. §6922(a)

20. 42 U.S.C. §9601, _et_ _seq_.

21. _United States v. NEPACCO_, 579 F.Supp. 823 (W.D. Mo. 1984); _United States v. Reilly Tar_, 546 F. Supp. 1100 (D. Minn. 1982); _Ohio v. Georgoff_, 562 F. Supp 1300 (N.D. Ohio 1983).

22. 42 U.S.C. §9604

23. United States v. Chem-Dyne, 572 F. Supp 802 (S.D. Ohio 1983); United States v. Wade, 546 F. Supp. 785 (E.D. Pa. 1982); City of Philadelphia v. Stephan Chemical Co., 544 F. Supp. 1135 (E.D. Pa 1982)

24. The total amount of the Superfund was increased last year to $8.5 billion.

25. 42 U.S.C. §9605; 40 C.F.R. Part 300

26. 42 U.S.C. §9601(14)

27. 42 U.S.C. §9607(a)

28. 42 U.S.C. §9604(c)(1)

29. 42 U.S.C. §9604

30. 42 U.S.C. §9604(c)(4)

31. 42 U.S.C. §9621

32. 42 U.S.C. §9622(g)

33. 42 U.S.C. §9622(e)

34. 42 U.S.C. §9607(a)(3) and §9601(35)

35. 42 U.S.C. §9613(c)

36. 42 U.S.C.§9603

37. 5 U.S.C. §552; 40 C.F.R. Part 2

38. 42 U.S.C. §9613(f)

HOW CLEAN IS CLEAN?
(WHAT CONSTITUTES THE CLEAN CLOSURE OF A HAZARDOUS WASTE LAND MANAGEMENT FACILITY?)

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BACKGROUND

The Hazardous and Solid Waste Amendments of 1984 contained a National Policy to treat, store and dispose of hazardous waste so as to minimize future threats to human health and the environment. One of the findings of the 1984 Amendments was that certain classes of land disposal facilities, specifically landfills and surface impoundments, cannot assure the long term containment of hazardous wastes. It was concluded that in order to avoid risk to human health and the environment, landfills and surface impoundments will be the least favored method of managing hazardous wastes in the future.

As part of the process of implementing this waste management strategy, the 1984 Amendments contained stringent requirements for all surface impoundments and landfills, which effectively force the closure of most of these facilities. Part 264 regulations require surface impoundments to:

(1) install a double liner and an associated leachate detection system (by November 1988);

(2) escrow closure and post closure costs; to provide sudden liability insurance of $1 million per occurrence and $2 million per aggregate, and non-sudden liability insurance of $3 million per occurrence and $6 million per year aggregate; and

(3) provide groundwater monitoring during the life of the facility and for 30 years after closure for those not closing "clean".

Clearly, the intent of these regulations was to force the closure of most surface impoundments and landfills within four (4) years of enactment of the 1984 amendments. However in order to close a land management facility to a degree to which it becomes deregulated (i.e., "clean") the owner/operator must remove not only the waste material but underlying contaminated soil and contaminated groundwater. For listed wastes such as (F006) electroplating sludges, achieving "clean" closure requires removal of underlying contaminated soils and groundwater to site specific background levels. Unfortunately in most instances this site specific level is zero or less than detection levels of present analytical procedures.

While the goals of this legislation are scientifically irrefutable (we agree that land management of Hazardous Waste is the least favorable solution), the present regulations (or interpretations of those regulations) make it almost impossible to "close a land management facility to the degree which present regulations require as 'clean'". Moreover, for most electroplating facilities, it is virtually impossible, financially to close "clean".

Consequently, a large number of owners and operators of land management facilities are facing a dilemma, a regulatory paradox: they cannot remain open, due to regulatory and financial constraints, nor can they close, due to regulatory and financial constraints.

According to EPA's hazardous waste data base, there were 1,338 impoundments at 981 interim status facilities across the U.S. as of September 10, 1985[1]. In Connecticut, where the authors have extensive experience, there are 86 impoundments which remain to be closed or retrofitted. Moreover, almost all of the 86 Connecticut impoundments mentioned above are associated with electroplating facilities.

There is little question that the majority of these facilities nationwide wish to close prior to November 1988 in order to avoid the expense and management requirements necessary to meet the 40 CFR 264 regulations for continuing use of land management facilities. The real question is how these facilities can close in a manner which will protect human health and the environment, and at the same time, at an affordable cost and in a way which takes into account the limited options available for disposal of hazardous electroplating wastes.

In short, the answer to the question of "How Clean is Clean?" may become the critical factor in determining the ability of land management facility owners and operators such as electroplaters to remain in business.

Using the authors' experience with Connecticut electroplaters who are at present in the midst of this dilemma, this paper attempts to probe the concept of "How Clean is Clean?" and to suggest possible alternate policies which will facilitate the intent of Congress and the wishes of land management owners/operators, that is, to close their land management facilities.

The following issues are considered key components in addressing "How Clean is Clean?":

(1) Listed versus Characteristic Wastes or what makes a waste hazardous;

(2) The effect of the wastes and residues on existing groundwater quality and present and future groundwater users;

(3) The limited availability of permitted secure landfills for waste disposal; and

(4) Economics

The following four (4) sections of this paper will explore each of the subjects listed above. The significance of these issues will then be illustrated in three (3) case histories. Finally, recommendations will be presented for what the authors consider a reasonable and implementable clean closure policy which is protective of human health and the environment.

LISTED VS CHARACTERISTIC WASTES (THE DOUBLE STANDARD)

When the Resource Conservation and Recovery Act Regulations were first promulgated in 1979, their intent was to immediately identify and regulate those hazardous waste products most likely to cause contamination problems if improperly disposed. To achieve this, the regulations identified both listed waste sources and characteristic wastes. Listed wastes, such as electroplating sludges (F006) and their residues were listed because they typically contained high concentrations of cadmium, hexavalent chromium, cyanide and nickel. Conversely, characteristic wastes were identified as those solid wastes which when subjected to a specific leaching test would discharge elements and compounds at a concentration 100 times greater than that listed in the National Primary Drinking Water Standards for eight (8) metals (arsenic, barium, cadmium, chromium, lead, mercury, silver and selenium) and 6 pesticides. These metals and pesticides were chosen because they already had defensible limits associated with them. An attenuation factor of 100 was considered adequate to account for the fixation, degradation, and dilution of these metals and compounds in the soil and groundwater between an existing sanitary landfill and a typical public drinking water supply.

The immediate double standard applied here and the consequent disadvantage in which this places electroplaters is that listed wastes (e.g., F006) require submission of a lengthy (and costly) delisting petition to have their wastes excluded from regulation. Any other metal finisher or industry simply has to perform an EP Toxicity Test on his wastes to determine if it is hazardous, and if it is not, it is immediately excluded from regulation. An example of this double standard is that while an electroplater with 0.1 ppm of trivalent chromium in his sludge would be regulated an industry with 4.9 ppm of hexavalent chromium in his characteristic waste is not.

The double standard also has significant ramifications on the issue of "How Clean is Clean?"

During closure of a listed waste land management facility, any underlying soil or groundwater which exhibits any concentrations of contaminants in the listed waste (e.g., for a F006 waste the contaminantsare Cd, Cr^{+6}, Ni and CN) above background (normally zero) must be removed. It has been our experience that the volume of underlying contaminated soils generated during closure of metal hydroxide lagoons is two to five times the volume of the metal hydroxide. Making matters worse, however, is that for listed wastes, all of the contaminated soil must be disposed of as a hazardous waste at a secure chemical landfill. This requirement has resulted in the need for secure landfill disposal of soils which exhibit metal concentrations less than drinking water standards.

Conversely, soils underlying a characteristic waste land management facility do not require removal if exhibiting EP Toxic concentrations less than 100 times the drinking water standards

Although the 1984 Amendments have left the listed and characteristic classifications in place, on June 13, 1986 a proposed regulation for 40 CFR 261 outlines a new approach in developing regulatory concentrations which are more realistic. Unfortunately, this proposal is for characteristic wastes only. The proposed method uses chronic toxicity reference levels (from published sources) combined with a compound specific dilution/attenuation factor (derived from application of a groundwater transport model) to calculate the regulatory threshold concentrations for individual toxicants. This method also accounts for exposures to humans by other than drinking water sources (i.e., food, air) in setting a regulatory limit for specific compounds.

It is realized that the purpose of the initial RCRA regulations was to quickly absorb into the regulatory system as many hazardous wastes as possible by listing waste types thereby requiring wastes such as electroplating sludges to be regulated wastes regardless of their constituents. However, it appears that a more sophisticated evaluation procedure is forthcoming for characteristic waste which provides a scientific basis for regulating a waste. Considering the significant impact on listed waste land management owners, why can't this new procedure be applied, if not for the waste itself, at least for underlying soils?

EFFECT ON GROUNDWATER

At the present time, federal regulations do not include an evaluation of existing ground water quality and use in determining the extent of underlying soil and groundwater removal to achieve "clean" closure. The State of Connecticut had been using a standard for clean closures of lagoons which had been less stringent for areas where groundwater was historically degraded or not used for public water supply. However, a recent EPA Region 1 letter to the State of Connecticut stated that, "Although perhaps relevant (groundwater classification system) in choosing priorities for DEP action, such a system is legally irrelevant in establishing closure standards."[2] It is clear that the intent of this finding was to direct the State of Connecticut to insist on removal of all contaminated soil and treatment of contaminated groundwaters below a listed (i.e., F006) hazardous waste site, down to background levels, instead of using their established practice of adjusting removal limits based on existing ground water quality and/or use.

It must be noted that the 1984 Amendments also make provisions for allowing higher concentrations of contaminants leaving a land management facility (264.94) based upon groundwater quality and quantity and the extent of current and future groundwater users. In addition, EPA's present Groundwater Protection Strategy recognizes that there are Class III (degraded) groundwater areas which will be evaluated for less stringent protection standards. If this is to be the case, the logical question is: Why can't the groundwater quality and use be considered in setting a realistic standard for removing the contaminated soil and groundwater beneath a land management facility to be closed? Certainly Connecticut and most other states have large areas where the groundwater will never be utilized for a public drinking water supply due to need, historical contamination, existing land use, recharge rates, and/or salt water intrusion. It seems an irresponsible use of electroplaters' financial resources and an unnecessary utilization of secure chemical landfill space to require excavation of soil to background levels when at some sites it is clearly not needed to protect human health and the environment.

LIMITED AVAILABILITY OF SECURE LANDFILLS

The most common method used in closing metal hydroxide lagoons is to dispose of the plating sludge and contaminated soil at a permitted secure chemical landfill. In other words, closure consists of removing hazardous wastes from one land disposal site for disposal at another, although both are considered likely to leak at some point in their operational or closure periods. It is important to remember that all contaminated soil below listed wastes, regardless of its hazard degree, is required to be sent to secure landfills. These landfills have a finite capacity, are often distant from the project site, and in some cases do not have the financial assurance or groundwater monitoring systems required by 40 CFR 264.

In 1985, there were only 27 hazardous waste landfills located in 15 states throughout the country with a total life expectancy of 15-19 years. Two of these facilities had no financial assurance mechanism and eleven had inadequate groundwater monitoring systems.[3] Admittedly, the prospects of expanding these facilities or opening new ones is limited by the 1984 Amendments which consider land disposal the least favored management option, and by local opinion which strongly opposes these types of facilities.

In Connecticut and other New England states, there are a very limited number of secure landfills available for disposal of closure sludges and soils. There are only two secure landfills within 375 miles of the center of Connecticut and they represent only 1% of the nationwide 60 million tons of permitted capacity. The life expectancies of these two facilities are 0.8 and 5.0 years.[3] There are 4 additional facilities with 8% of the nationwide capacity within 500 miles of Hartford, 6 within 750 miles (27% of total capacity), and the remaining landfills are greater than 1000 miles away.

In 1983, Connecticut alone produced approximately 105,000 tons of metal wastes. Of this total 27,500 tons were landfilled, 33,900 tons were dewatered in surface impoundments, and 37,000 tons were subject to aqueous treatment. If Connecticut exported all its annual generation of landfilled and surface impoundment wastes to the two closest landfills, it would fill them itself within 10 years. Considering that Connecticut has 86 land disposal facilities which may need to be closed, there is a tremendous amount of sludge and more soil which will need to be sent to secure landfills, thereby further decreasing their life expectancy. It seems a poor choice of a limited resource to require low level contaminated soil to be disposed of at these secure landfills if it is not needed to protect human health and the environment.

ECONOMICS

It should be stated at the outset that hazardous waste disposal costs have increased dramatically over the past 3 years, and undoubtedly will continue to escalate in the future. In addition transportation costs to remaining secure landfill sites will increase as more sites close, and wastes must be sent farther away.

A recent survey of 18 hazardous waste management firms[4] indicated that they received 6.38 million metric tons of wastes in 1985 of which 45% went to landfills for disposal. Prices for landfill disposal are reported to have increased between 30 and 100 percent between 1984 and 1985. On the average, respondents said they anticipated a 20-25 percent annual growth in revenues in the future, a significant portion of which is attributed to the closure of landfills and surface impoundments.

At present, secure landfill disposal costs of metal plating wastes from Connecticut companies averages $95-$135/ton plus bulk transportation costs of $75-$90/ton, for a total of $170-$225/ton. A recent report prepared for the Connecticut Hazardous Waste Management Service[3] estimated that 1990 disposal costs (excluding transportation) for a Connecticut based secure landfill would be $269-294/ton.

Clearly, the cost of metal plating sludge disposal is expensive now (approximately $200/ton) and, by reliable accounts, will continue to escalate in the future (reaching $300/ton within 5 years) as more secure landfills close.

As discussed previously and specifically described in the following case histories, present "clean closure" requirements significantly increase the volume of material generated in a closure which must be secure landfilled. The associated additional costs to many land management facility owners are unanticipated and for the small electroplating shop, an impossible financial burden.

CASE HISTORIES

The three (3) companies selected for case histories include two large job plating shops and one large consumer products manufacturer who have operated unlined surface impoundments for 10-15 years and are now attempting to close clean prior to November 1988. Although each of these facilities has expended extensive sums of money in attempting to close clean, at present none of them are considered to meet the 40 CFR 264 criteria which would allow them to be classified as such and qualify as non-regulated facilities.

COMPANY X

The first company examined in this report is a 50 year old plating firm located in a heavily industrialized city. Processes include electroplating, anodizing, and black oxidizing operations. Prior to November 8, 1985, the company had discharged its metal hydroxide sludges to on site dewatering and sludge impoundments. Since then, approximately 240 cubic yards per year of dewatered F006 sludges are shipped off site for secure landfill disposal.

This Company evaluated the costs of closing in place versus closing clean and found that it was more economical and desirable to close clean. The closure plan that was approved by the Connecticut DEP called for removal and secure landfill disposal of all sludges and contaminated soil which exhibited EP Toxicity metal concentrations greater than 30 times Drinking Water Standards; removal and local landfill disposal of all contaminated soil with 10-30 times Drinking Water Standards; and leaving the remainder of soil in place subject to groundwater monitoring for at least five years.

The State of Connecticut lost its authorization to implement the RCRA program in January 1986 which resulted in the re-review of this Closure Plan by EPA. Subsequently, EPA interpretation of clean closure for this facility will require that all contaminated soil and groundwater be removed and/or treated. The costs of the three (3) options that the Company must now consider (closure in place, non clean closure, clean closure) are summarized in Table 1. The results of sludge and contaminated soil testing conducted at the facility are included in Table 2.

As indicated in Table 1, EPA clean closure is the most expensive option for the following reasons:

(1) Approximately 975 cubic yards of contaminated soil with the low levels of cadmium and nickel shown on Table 3 will need to be shipped to a secure landfill for disposal at a cost of $245,000. This minimally contaminated soil is equivalent to 4 years of the Company's sludge generation rate and is to be added to the equivalent of 12 years of sludge and hazardous soil already required to be shipped off site.

(2) Groundwater treatment will be needed for an estimated 5 years to remove residual groundwater contamination. This is required even though, (1) due to historic contamination in this area background water quality samples have cadmium and nickel levels in excess of drinking water standards; (2) there are no public water supply wells within one mile of the site; and (3) salt water intrusion is present due to the proximity of Long Island Sound.

Closure in place is the least expensive alternative. The most expensive item here is the $65,000/year for obtaining non sudden release insurance. Of more concern, however, is the uncertain future availability of this type of insurance. The company also had a concern that land disposal regulations would become more difficult to meet in the future. For these reasons closure in place was not selected for use at this facility.

The "DEP Alternative" which the Company would like to pursue insures the secure landfill disposal of clearly hazardous wastes, while allowing those soils which are well below characteristic standards to be shipped to a local landfill as a solid waste. Precipitation infiltrating through the sludge beds will be diluted 20:1 by the flow passing under the impoundment. This dilution will allow the groundwater downgradient of the closed facility to have contaminants present at no more than half of accepted drinking water standards. This condition will be verified by the monitoring of the Company's groundwater wells over the 5 years after closure.

COMPANY Y

Company Y is a manufacturer of consumer products and is located in a rural section of Connecticut. A state road runs along the eastern boundary of the site and a river runs parallel 100' farther east. Operations at the facilities include nickel and trivalent chrome plating of metal parts. Prior to August 1985, these chemically treated wastewaters were discharged to an unlined surface impoundment for sludge dewatering. This practice was eliminated to ensure closure of the lagoon prior to November 1985. Wastewaters are now treated by ion exchange units for removal of nickel and trivalent chrome.

In September 1985, operations for final lagoon closure began at the plant in accordance with a Closure Plan filed with the Connecticut Department of Environmental Protection (DEP) in April 1985. Approximately 315 cubic yards of hazardous sludge and soil with the characteristics listed in Table 3 were removed and sent to the Stablex facility in Canada for secure landfill disposal. Another 400 cubic yards of contaminated soil (see Table 3 for charcteristics) were removed and taken to a local landfill for disposal.

Four (4) groundwater wells have been monitored at the Company since August 1982. These wells include one (1) upgradient well (MW-1) and three (3) downgradient ones. In March 1986, sampling of these wells indicated that the highest downgradient concentrations for nickel and total chromium was 0.02 milligrams per liter (mg/l), total cyanide 0.05 mg/l, while cadmium was undetected. (See Table 4.)

Since the soil left in place has not been removed down to background levels the Company is now faced with the dilemma of either removing additional soil or closing as a landfill. The costs of these alternatives and the closure costs that the Company has incurred to date are itemized in Table 5.

It is evident that to close as a landfill is just too costly to be considered a viable alternative. Clean closure is approximately twice as expensive as costs incurred by the Company to date, solely due to the costs of secure landfill disposal of all contaminated soil. It is questionable what benefits are present to justify the additional expenditure of $125,000 over the company's present closure cost.

In this case, the only groundwater user in the immediate area is the Company itself which pumps 250 gallons per million (gpm) from MW-3 for plant uses. As indicated in Table 4, the concentrations of contaminants in these wells does not approach adopted or proposed drinking water standards. There is a public water supply well located one-quarter (¼) mile northeast and upgradient of the facility. Considering that the groundwater contours in this area clearly indicate flow away from the public well and towards the river located only 350 feet north east of the site, the public well will not be affected.

After groundwater leaves this Company's property, it travels underneath a State Highway and into a river with a drainage area of 230 square miles, an expected average daily flow of 690 cubic feet per second (cfs), and a 7 day, once in 10 year low flow of 35 cfs. Dilutedgroundwater flow leaving the lagoon is estimated at 0.03 cfs (21,000 gallons per day (gpd). Therefore under worst case ($Q_{7/10}$) conditions, the water leaving the lagoon area would be diluted in the river at a ratio of 1160:1 (35.0:0.03). Without performing the mathematics, it is clear that none of the contaminants listed in Table 4 will have the slightest impact on the river, thereby diminishing its quality or use.

As a final point, it is interesting to note that this same Company has an NPDES permit which allows it to discharge 22,000 gpd of treated electroplating wastewater with average concentrations of 1.0 mg/l nickel and 1.0 mg/l total chromium to the same river which receives its groundwater flow.

COMPANY Z

The final company selected for review is a large job plating shop whose plating processes include copper, nickel, silver, chromium, tin and gold. The company is located in an industrialized city, about 300 feet east of a major river. Area groundwaters have been degraded due to past practices by industries throughout the area. There are no public water supply wells within one mile of the site.

Since the early 1970's this company has sent 80,000 gpd of treated metal plating wastewater to this lagoon for the precipitation of metal hydroxide sludge. Approximate dimensions of the lagoon were 90 feet by 40 feet. The treated wastewaters are now mechanically dewatered.

At the time of closure, this impoundment had approximately 45,000 gallons of standing liquids and 60 cubic yards of sludge removed for treatment and secure landfill disposal. The Company also had to remove 400 tons of contaminated soil for secure landfill disposal. The limit of excavation was determined by comparing composite samples of the lagoon bottom to background levels of hazardous constituents found in soils in a wooded, undeveloped section of the property. The cost of this removal and disposal operation was $120,000.

Four (4) groundwater wells have been in place at the facility since June 1984. Results of the sampling of these wells prior to closure are included in Table 6, with MW-1 representing the upgradient well. Three of the four parameters for which this sludge is listed (cadmium, chromium and nickel) are at or just above detection limits. Total and amenable cyanide is present in elevated levels approximately twice as high as the usually accepted drinking water limit of 0.2 mg/l. The need for groundwater treatment at this facility, considering the removal of contaminated material, the lack of groundwater users, and the area hydrogeology has not been established in the authors' opinion.

Groundwater flow across the Company's property is southwest towards the river located 300 feet west of the plant and flowing south. The overlying surficial material is a mixture of sand, gravel and silt, approximately 50 feet thick and with a field measured hydraulic conductivity of 1.6 feet per day. The precipitation leaching through the lagoon is estimated at <0.005 cfs and is diluted 14:1 with the underlying groundwater flow, thereby serving to bring all contaminants within Drinking Water Standards. As mentioned earlier there are no public wells within one mile of the site.

The adjacent river has a drainage area of over 200 square miles. Average daily flow in the river is 380 cfs with $Q_{7/10}$ of 28 cfs. The result of this facility's groundwater discharge is a worst case ($Q_{7/10}$) dilution rate of 4000:1 (40,000:1 average) which provides ample dilution to prevent any contaminants from posing a health problem in the river. Also as with the previous Company Y, Company Z is allowed to discharge 80,000 gpd of treated plating wastewater with metal concentrations 3-50 times higher than in its groundwater discharge to the same river which receives its groundwater flow.

CONCLUSIONS AND RECOMMENDATIONS

The issues presented in this paper illustrate several problems associated with the clean closure of existing surface impoundments. It is, of course, impossible within the limits of this paper to adequately address all of the complexities associated with each issue. Consequently, some simplification has been made.

There is however, no simplification of the problem facing many small electroplaters who wish to close their land management facilities. The issues and general recommendations of this paper are summarized below:

(1) The need for secure landfill disposal of contaminated soils should be based on hazard potential as defined by the results of an EP Toxicity test and not arbitrarily required because the source was a listed waste. Preparation of a lengthy delisting document is not considered a viable alternative for most plating companies. Due to the minimum finite capacity of existing secure landfills and the high costs for disposal at these facilities, it is imperative that there be a more scientific basis for requiring disposal as hazardous wastes.

(2) The limit of contaminated soil removal should be based on the potential health hazard and effect on the environment associated with leaving some contaminated soil in place. It is extremely difficult, costly and in some cases virtually impossible to remove all contaminated soil down to background levels. The decision on where to stop excavation should be based on the leaching potential of the soil left in place, the proximity of existing groundwater users, the potential for aquifer use in the future and what effect there may be on adjacent streams. Use of these factors in making a decision on the extent of soil removal may likely allow some slightly contaminated soil to remain in place as part of a clean closure.

(3) Groundwater discharge limits associated with a closed surface impoundment should be assigned on a realistic basis, again considering background water quality, and the existing and potential aquifier uses. It is unrealistic to require drinking water limits to be met by a company when historic contamination of the aquifier far exceeds those limits; or salt water intrusion prohibits use of the aquifier as a well supply; or the aquifier cannot provide sufficient quantities of water for public use. Higher limits are warranted for some groundwater discharges from closed surface impoundments considering the factors mentioned above.

In conclusion while the intent to close out unlined hazardous waste surface impoundments is an excellent intention, it is necessary to temper that goal with realistic closure standards so as to allow for the practical implementation of this goal.

TABLE 1

PRESENT WORTH
CLOSURE COSTS
COMPANY X

ITEM		OPTIONS	
	CLOSURE IN PLACE	EPA CLEAN CLOSURE	DEP CLEAN CLOSURE
Double liner & leachate collection	$ 50,000	- - - -	- - - -
Insurance	638,170	- - - -	- - - -
Groundwater monitoring	58,900	- - - -	$ 20,000
Annual maintenance	19,600	- - - -	- - - -
Groundwater treatment (5 years)	- - - -	$ 75,000	- - - -
Excavation & secure landfill disposal costs	- - - -	971,250	712,950
Excavation & sanitary landfill disposal costs	- - - -	- - - -	18,750
Fill	- - - -	37,000	37,000
TOTALS	$ 766,670	$ 1,083,250	$ 768,700

i = 8%
n = 20 years

TABLE 2

SOIL & SLUDGE SAMPLE RESULTS
COMPANY X

PARAMETER	SLUDGE	SLUDGE/SOIL INTERFACE	2' BELOW SLUDGE	EP TOXICITY CHARACTERISTI
ARSENIC	<0.1		- -	
BARIUM	22.6	0.1-0.92	- -	100.0
CADMIUM	18.5	0.1-1.43	0.1-0.29	1.0
CHROMIUM$_{+6}$	<0.01	- -	- -	5.0
CHROMIUM$_{TOTAL}$	230.0	<0.1	- -	5.0
LEAD	18.8	<0.1	- -	5.0
MERCURY	<0.1	- -	- -	0.2
NICKEL	670.0	0.11-10.7	0.1-1.09	15.0*
SILVER	1.92	- -	- -	1.0
SELENIUM	<0.1	- -	- -	
CYANIDE$_{TOTAL}$	<0.1	- -	- -	NO STD*

* 100 TIMES NO ADVERSE RESPONSE LEVEL OF 0.15 MG/L

"All units in mg/l.

TABLE 3

SLUDGE/SOIL CHARACTERISTICS
COMPANY Y

PARAMETER	SLUDGE	CONTAMINATED SOIL	SOIL LEFT IN PLACE
CADMIUM	<0.02	<0.02	<0.02
CHROMIUM$_{TOTAL}$	0.18	<0.02	<0.02
COPPER	0.17	<0.1	<0.1
NICKEL	13.688.0	0.49-11.20	0.72

"All units in mg/l."

TABLE 4

MONITORING WELL RESULTS
COMPANY Y

PARAMETER	MW-1	MW-2	MW-3	MW-4
pH	6.27	7.28	6.65	6.83
Calcium	1.31	33.9	5.55	35.7
Cadmium	<0.01	<0.01	<0.01	<0.01
Chromium, total	0.01	<0.01	<0.01	<0.02
Copper	<0.01	<0.01	0.02	<0.01
Iron, dissolved	0.10	0.13	0.15	0.11
Magnesium	0.87	21.9	3.13	20.9
Manganese	<0.01	<0.01	<0.01	<0.01
Sodium	1.73	6.24	8.49	41.2
Zinc	0.01	<0.01	0.79	<0.01
Nitrate-N	<0.01	0.94	0.29	0.63
Nitrite-N	<0.005	<0.005	<0.005	0.007
Cyanide, total	0.05	<0.01	<0.01	<0.01
Chloride	4.5	9.0	22.5	53.9
Sulfate	8.7	10.0	11.7	43.7
Dissolved Solids	29	158	65	326
Hardness	4.4	44.0	8.8	44.0
Alkalinity	4.0	82.0	1.6	42.0
Ammonia-N	<0.05	<0.05	<0.05	<0.05
Sulfite	<0.1	<0.1	<0.1	<0.1
Specific Conductance umhos/cm	31	170	70	350

All results in mg/l.

TABLE 5

CLOSURE COSTS
COMPANY Y

ITEM	COSTS TO DATE	LANDFILL CLOSURE	CLEAN CLOSURE
Insurance	- - -	$ 638,170	- - -
Groundwater monitoring	$ 20,000	58,900	- - -
Annual maintenance	- - -	19,600	- - -
Excavation & secure landfill disposal costs	82,700	82,700	$ 236,250
Excavation & sanitary landfill disposal costs	10,000	10,000	- - -
Fill	7,150	7,150	7,150
TOTALS	$ 119,850	$ 816,520	$ 243,400

TABLE 6

MONITORING WELL RESULTS
COMPANY Z

PARAMETER	MW-1	MW-2	MW-3	MW-4
Cadmium	nd<0.02	nd<0.02	nd<0.02	nd<0.02
Total Chromium	nd<0.02	nd<0.02	nd<0.02	nd<0.02
Copper	nd<0.02	0.46	0.62	nd<0.02
Iron	0.33	5.60	14.50	0.24
Lead	nd<0.02	nd<0.02	nd<0.02	nd<0.02
Nickel	nd<0.02	nd<0.02	nd<0.02	nd<0.02
Silver	nd<0.02	0.14	0.03	nd<0.02
Tin	nd<0.05	nd<0.05	nd<0.05	nd<0.05
Zinc	nd<0.02	0.13	0.84	0.04
Cyanide (total)	nd<0.01	0.34	0.24	0.06
pH	6.36	9.38	9.92	7.04
Cyanide (amenable)	nd<0.01	0.34	0.24	0.06

FOOTNOTES

1 Interim Status Surface Impoundment Retrofitting Variances, Labat-Anderson, Inc., Arlington, Virginia, July 1986.

2 Letter from Michael R. Deland, Region 1 Regional Administration to Stanley Pac, DEP Commissioner, March 13, 1986.

3 Connecticut Hazardous Waste Management Plan: 1985-2005, The Connecticut Hazardous Waste Management Service, January 1, 1986.

4 Hazardous Materials Intelligence Report, World Information Services, Cambridge, Mass, December 12, 1986.

INSTALLATION OF A NEW NICKEL/CHROMIUM PLATING FACILITY

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DESIRE FOR A NEW PLATER MACHINE.

The facility manufactures hand tools such as wrenches, ratchets, adjustable wrenches and, wrench set accessories. After forging,shot blasting,machining,and polishing,the pieces are racked and plated in a bright nickel/hex chrome electroplating process.

The existing machine was built in 1969 and used in another plant before being set up in Wichita Falls in 1980. It was a fixed cycle, elevator type machine. A rack strip facility was located beside it. The machine capacity was 4.5 square feet per minute.

The machine penalized our operation in the following ways:

1. We couldnot repair corroded tanks with out excessive down times and labor premiums. We expected imminent failure of our chrome tank at an expected cost of $26104 plus $12991 estimated cost to make up lost production.
2. Elevator flexing due to extensive corrosion was causing 10 wrecks per year at a cost of $41463 per year. The replacement would cost $58305 plus one week down time.
3. We knew these costs would probably occur,but under accounting rules cost avoidances are not counted on return on investment.
4. There were no options on this style of plater to try new processes nor could we add or subtract significant plating thicknesses.
5. There was no way to install water saving rinse tank configurations.
6. The lack of water saving contributed to increased waste treatment costs.

A programmable hoist type was selected for procurement. This type would provide the flexibility for tank repair, new process introduction, and waste treatment savings.Additionally, the location selected would provide a more efficient production flow.At the same time provision for future added capacity would be provided.

SYSTEM COST ANALYSIS

The new production rate would eliminate one shift.The waste treatment system could be turned down to 10 hours per day:

(32.3 kwh x 16hrs -32.3 kwh x 10 hrs)x240 days x
$.050/kwh = $2326.

A change from electric tank heating to steam tank heating was contemplated.The utility savings are given.

Cost of electricity = $.05 / kwh
Cost of natural gas = $4.33 / 1000 cubic feet
Steam system efficiency with natural gas = 60%
Electric heat efficiency = 100%
Watts X 3.41 = btus per hour conversion.
Natural gas nominally has 1000 btus per cubic foot.

1KW X 3.41 btus X $4.33/.6/1000btus/1000 cu.ft.=$.024/hr/kw
$.05/kwh - $.024/kwh = $.026 difference.
In a one shift year this would be $.026 x 8 x 240
= $49.92/per kwh.per year or 56.6 av. kw x $49.92
= $2825/yr estimated savings.

RINSE CALCULATIONS.

Rinse water savings were calculated based on counter flow tanks and metered control of rinse water.The existing plating rinse flow was estimated from actual plater operation. The original rinse arrangement had been modified .The acid rinse was only one tank. The other tank was turned into a "sour dip" with sulfuric acid. The original nickel counter flow tanks were reduced to one.The first tank had become a dragout tank and the third tank was made into a chromic acid pre-dip tank. The draining of this last tank periodically was a large load on the waste treatment system. The rinse water rate was arbitrarily set by the plating foreman.

A spread sheet was devised to show these costs. FIG. 1.These take a little more time to first organize,but then become very fast to show results with different parameters.The results indicated that 70_% less water would provide better rinsing for 37 % more production and save $_6460 per year in water bills alone,not to mention the increased life of the pre-dip tank and decreased water load on the waste treatment system.

FIGURE 2 shows the formulas for the rinse parameters:

* =	multiplication	+ =	addition
/ =	division	- =	subtraction
^ =	exponent		

A letter followed by a number is the cell location to be operated on.

ELECTROLESS NICKEL (Figures 3 and 4)

The cost determination of the electroless nickel process was found to be very complex and depended on vendor supplied curves and tables. A more fundamental approach using a spread sheet was devised. It is based on the weight of nickel lost from the bath and deposited on the parts. The deposition rate of nickel in a bath has an exponential relation to the nickel concentration. As the nickel is plated on the part,the rate slows. Adding new solution to keep the concentration of nickel constant or in a small range allows a constant rate production process. This spread sheet is shown for 7.5 tank turnovers and is for assigning chemical costs to a specific product. No allowances are made for the "Pandoras Box" array of problems that come with this process. The ".5 " tank turnover is for the last one where the tank is allowed to run down without an add before discarding.

The rate of deposition used is 0.0007" per hour (.7mils/hr.). The range of nickel concentration used is 0.4 oz./gal per turnover. It is very important to list the EN surface area,which includes recesses and holes not reached in electroplating.

The program was used for preliminary cost estimates but has not been compared in a plating operation.

TRIVALENT CHROME PROCESS

The waste treatment economies realized by changing from a hexavalent chrome process to a trivalent chrome process are significant:

1. The cost of sodium metabisulfite reducing agent and the sulfuric acid PH adjuster are eliminated. The yearly cost in our plant was $1600.
2. The concentration of chrome metal in a trivalent bath is 5% of the hexavalent chrome metal in a chromic acid bath. Since the dragout quantity is the same, the waste treatment process can be reduced 95%.The projected yearly savings in our plant was $19400.
3. The current requirements of trivalent chrome is 43% of the hexavalent chrome process.The projected yearly saving in our plant $1880.

The detail calculations for the chemical reactions involved are explained in ref.1.

FACILTY ADAPTATION

There were six major facility projects to be constructed to accomodate the new plating machine:

1. An electrical 3 phase power bus and single phase transformer.
2. A concrete curb and slab for the plater base.
3. A waste treatment connection pit.
4. A roof top blower base and roof penetration.
5. A steam boiler and piping system.
6. A water supply.

The major problem with these was the scheduling. On the one hand the facility design has to be coordinated with the plater design that was in progress and on the other it must be in place when the equipment arrives; Certainly the concrete and the roof penetrations,while the rest should be completed with minimum interference with the plater installation.A seventh project of moving all the things that were located on the future site turned out to be one of the toughest jobs of all!

The same project can appear simple or complex depending on the people doing it. Experienced, competent engineers and technicians working with complete plans seem to get it done with no fuss and it works the first time. An important adjunct to this is to insist on National and Local construction code compliance in every detail.These codes are the boiled down essence of good practice over the years (Shades of Little Abner and Kickapoo Joy Juice!).

An important area was cost control. There are bound to be deviations from the agreed work. The important thing is to write the descriptions and cost of the deviations as they occur and make sure they are mentioned on the invoices.

All seven projects were accomplished in time with no major glitches. One cost reduction of note involved the steam system.The steam load was just over 4 million btus/hr. The design called for a 15 psi steam boiler to an adjacent plating machine. The new location of the plating machine was 200 feet away.An analysis showed that a 90 psi boiler with a 3" pipe and pressure reducing valve was much more economical than a 200 feet run of 6" pipe.

INSTALLATION

The installation of this complex machine was mostly without incident.We mention two items of interest to future installations:

1. The triple rinse tanks were one tank with non load carrying partitions. The partitions were perfectly straight until they were filled with water; then they bowed drastically. It was thought that the tanks were filled unevenly and caused pressure bulges. The tanks were drained and stiffener angles were installed.This solved the problem. An examination of the girth beams showed they were not fastened to the tank walls, but just acted to hold in the pressure bulging action.It is believed here that the shorter side, which supports the partitions,tends to bulge inward in response to the corner rotation, which is in response to the greater strain in the longer side. The way to go is to fasten these girth beams to the short tank wall and get back the tank width taken by the stiffener angles.
2. The above caused us to examine the drainage connections. Each partitioned section drained through a valve and into a drain pipe alongside of the tanks.Obviously the furthest tank would drain slowest.An arrangement was devised so that the center tank fed into a cross first and then valved into the header. The end tanks were then valved and routed into the cross.If all valves are open,the tanks drain evenly.When filling, the header valve is closed but the end tank valves are left open. All three tank sections have a common pipe and fill evenly.

OPERATION

At some time it becomes necessary to find out the actual performance of a programmed hoist. The following procedure can be used very effectively to determine exactly what the hoist is doing. The speed, the delays, the effects of light and heavy loads, are all displayed on one record and at one time.

Program modifications can be done right the the first time with this aid.

A strip recorder, a clamp on current transformer, and an AC current module for the recorder are required.

Figure 5 shows the connections. A set of long leads are interposed in one output phase of each motor contactor,such as fast traverse, slow traverse, hoist lift and drop slow, and hoist lift and drop fast.

These long leads are brought together and the current transformer loop placed around them.Since only one of these contactors can be on at one time, a complete time and displacement record can be made. A sample is shownin FIG.6.

A record made when everything is working can be compared later to see if hoist performance has changed.Other records for programming or exact solution times are useful.

Here is a list of events from the sample in FIG.6:

A. Hoist accelerates without a rack.
B. Hoist traverses at constant speed
C. Hoist approaches station and shifts to low speed.
D. Hoist stops.
E. Hoist lifts rack of parts.
F. Hoist pauses for drip.
G. Hoist accelerates with a rack.
H. Hoist traverses at constant speed with a rack.
1. Hoist approaches station and shifts to low speed
J. Hoist pauses for rack sway decay.
K. Hoist drops at high speed.
L. Hoist goes to slow speed for immersion.
1. Hoist stops waits for next instruction.

CONCLUSION.

The highlights of a 570 sq.ft per hour plating machine procurement have been described.The machine is in service and the crew is gradually bringing the system up to full production of bright nickel and decorative chrome plate on hand tools.

ACKNOWLEDGEMENTS

1.Waste Treatment and Recovery----OMI International Corp.
Environmental Services
Warren, Michigan
2.Technical Bulletin------------ Frederick Gumm Chemical
Co. Inc,
Lyndhurst, New Jersey
3.The Art and Science of Rinsing--J. B. Mohler
AES Lecture Series 1973

```
   :           A            ::    B    ::    C    ::    D    ::    E    :
 1: Rinse Flow Calculations            -Planned New Plater
 2: --and Water Savings----
 3: --file:rinsetnk.aes----OLD         ---OLD------NEW---
 4:-----DESCRIPTION--------Plater      --RACKS----RACKS--
 5:
 6:  CHROME RINSE TANKS(CF)        3        3        3
 7:  NICKEL RINSE TANKS(CF)        1        3        3
 8:       STRIP RINSE TANKS        2        3        3
 9:    ACID RINSE TANKS(CF)        1        2        2
10:    SOAP RINSE TANKS(CF)        2        2        2
11:  PRODUCTION (RACKS/HR.)       58      104      104
12: RACK FRAME SQ. FT.(OLD)     3.31     3.31
13:  RACK FRAME SQ.FT.(NEW)                        4.12
14: PRODUCT/RACK (SQ.FT)OLD      4.5      4.5
15: PRODUCT/RACK (SQ.FT)NEW                         5.5
16:DRAGOUT PRODUCT ML/SQ.FT       12       12       12
17:   DRAGOUT RACK ML/SQ.FT      8.7     10.2     10.2
18:    TOTAL RINSE SQ.FT/HR   452.98   812.24  1000.48
19:  CR., & NI.RINSE RATIOS   100000   100000   100000
20: SOAP & ACID RINSE RATIO      750      750      750
21:   DRAGOUT/RACK  GALLONS .0218750 .0231868 .0285400
22: ANY PROCESS DRAGOUT GPM .0211459 .0401904 .0494694
23: RINSE FORMULA ---------
24:     GPM=R^1/TNK*DRAGOUT
25:        WATER REQ. NI GPM 2114.587 1.864759 2.287370
26:         WATER REQ.CR GPM .9811275 1.864759 2.287370
27:ACT WATER NI. OLD PLATER        6
28:ACT WATER ACID OLD PLTR.        6
29:  ACT WATER STRIP & SOAP        4
30: WATER REQ.ACID,SOAP GPM .5791034 1.100660 1.354775
31:     WATER REQ.STRIP  GPM        4 1.864759 2.287370
32:    TOTAL WATER REQ. GPM       20 7.795598 9.571660
33:   WATER COST PER GALLON     .002     .002     .002
34:  COST 10HR/DAY 240 DAYS           2245.13  2756.64
35:  COST 16HR/DAY 240 DAYS  9216.00
36:   PERCENT SAVINGS WATER                          70
37: PERCENT MORE PRODUCTION                          37
38:
39:                         FIGURE 1.
```

```
  :           A           ::          B          ::          C           ::          D           :
 1: Rinse Flow Calculations                         -Planned New Plater
 2: --and Water Savings----
 3: --file:rinsetnk.for----OLD                      ---OLD---               ---NEW---
 4:-----DESCRIPTION--------Plater                   --RACKS--               --RACKS--
 5:
 6:   CHROME RINSE TANKS(CF) 3                      3                       3
 7:   NICKEL RINSE TANKS(CF) 1                      3                       3
 8:        STRIP RINSE TANKS 2                      3                       3
 9:     ACID RINSE TANKS(CF) 1                      2                       2
10:     SOAP RINSE TANKS(CF) 2                      2                       2
11:   PRODUCTION (RACKS/HR.) 58                     104                     104
12:  RACK FRAME SQ. FT.(OLD) 3.31                   3.31
13:   RACK FRAME SQ.FT.(NEW)                                                4.12
14:  PRODUCT/RACK (SQ.FT)OLD 4.5                    4.5
15:  PRODUCT/RACK (SQ.FT)NEW                                                5.5
16:DRAGOUT PRODUCT ML/SQ.FT 12                      12                      12
17:    DRAGOUT RACK ML/SQ.FT 8.7                    10.20                   10.20
18:     TOTAL RINSE SQ.FT/HR B11*(B12+B14)          C11*(C12+C14)           D11*(D13+D15)
19:   CR., & NI.RINSE RATIOS 100000                 100000                  100000
20:  SOAP & ACID RINSE RATIO 750                    750                     750
21:    DRAGOUT/RACK  GALLONS (B12*B17+B14*B16)/3785 (C12*C17+C14*C16)/3785  (D13*D17+D15*D16)/3785
22:  ANY PROCESS DRAGOUT GPM B11*B21/60             C11*C21/60              D11*D21/60
23: RINSE FORMULA ---------
24:      GPM=R^1/TNK*DRAGOUT
25:        WATER REQ. NI GPM B19^1*B22              C22*C19^.3333           D22*D19^.333
26:         WATER REQ.CR GPM B22*B19^.3333          C22*C19^.3333           D22*D19^.333
27:ACT WATER NI. OLD PLATER 6
28:ACT WATER ACID OLD PLTR. 6
29:   ACT WATER STRIP & SOAP 4
30:  WATER REQ.ACID,SOAP GPM B20^.5*B22             C20^.5*C22              D20^.5*D22
31:     WATER REQ.STRIP  GPM 4                      C25                     D25
32:     TOTAL WATER REQ. GPM B27+B28+2*B29          2*(C25+C30)+C31         2*(D25+D30)+D31
33:    WATER COST PER GALLON 20/10000               20/10000                20/10000
34:   COST 10HR/DAY 240 DAYS                        10*60*C32*240*C33       10*60*D32*240*D33
35:   COST 16HR/DAY 240 DAYS 16*60*B33*240*B32
36:    PERCENT SAVINGS WATER                                                ((B35-D34)/B35)*100
37:  PERCENT MORE PRODUCTION                                                (((D11*10*5.5)/(B11*16*4.5
38:
39:
```

FIGURE 2.

```
 :          A          :: B :: C :: D :: E :: F :
 1:ELECTROLESS NICKEL
 2:6-11-86FILE:PLTENUM.aes
 3:PLATER CAPACITY
 4:ASSUMED EFFICIENCY   100%
 5:SQARE FEET PER RACK        5.5
 6:SQ.FT.PER RACK EN           11
 7:RACKS PER CARRIER BAR        8
 8:CARRIER BARS PER HOUR       12
 9:TANK GALLONS               912
10:
11:EN CALCULATIONS
12:TIME IN EN MIN.             10
13:THICKNESS EN IN.      .0001167
14:CUBIC IN. NI PER HOUR 17.74080
15:OUNCES OF NI.PER HOUR 82.03346
16:RANGE NI.CONC.OZ/GAL        .4
17:HRS FOR TANK ADD REF. 4.446657
18:TANK TURNOVERS               7
19:7.5 TANK TURNS.(HRS)  73.36984
20:COST "A" COMP./GAL.         16
21:COST "C" COMP./GAL.         11
22:COST "B"OZ/GAL.             16
23:CONC.NI."C"OZ/GAL          8.8
24:MAKEUP TANK GAL "C"   91.19367
25:MAKEUP TANK GAL "A"   91.19367
26:DEIONIZED WATER GAL.  729.5493
27:COST FOR MAKEUP        2462.23
28:ADD TANK GAL.  "C"    91.19367
29:ADD TANK GAL.  "B"    91.19367
30:TOTAL ADDS "C"        638.3557
31:TOTAL ADDS "B"        638.3557
32:COST FOR ADDS         17235.60
33:TOTAL COST 7 TURNS    19697.83
34:OZ NI 7.5 TURNS       6018.782
35:COST PER OP HOUR      268.4731
36:EXPERIMENT TUBES               X40A      X40B      X40C      X40D
37:
38:LENGTH                            1.18     2.375      1.93      3.25
39:EN AREA                           6.13     12.51     13.13     22.46
40:PCS. PER RACK                      220       110       110        64
41:YEARLY DEMAND                    18768      9456     20952      8220
42:RACKS TO PLATE/YR.                  85        86       190       128
43:MACHINE HRS FOR BATCH              .89       .90      1.98      1.34
44:HOURS IN EN TANK                   .76       .78      1.81      1.21
45:COST OF EN PER PART           .0108227  .0220867  .0231814  .0396537
46:
47:
48:                               FIGURE 3
```

```
  :         A          :: B ::        C        ::        D        ::        E        ::        F        :
 1:ELECTROLESS NICKEL
 2:6-11-86FILE:PLTENCUM.JUN
 3:PLATER CAPACITY
 4:ASSUMED EFFICIENCY    100%
 5:SQARE FEET PER RACK    5.5
 6:SQ.FT.PER RACK EN     B5*2
 7:RACKS PER CARRIER BAR  8
 8:CARRIER BARS PER HOUR  12
 9:TANK GALLONS          133*66*24/1728*7.48
10:
11:EN CALCULATIONS
12:TIME IN EN MIN.       10
13:THICKNESS EN IN.      B12/60*.0007
14:CUBIC IN. NI PER HOUR B6*B7*B8*144*B13
15:OUNCES OF NI.PER HOUR B14*.289*16
16:RANGE NI.CONC.OZ/GAL  .4
17:HRS FOR TANK ADD REF. B9*B16/B15
18:TANK TURNOVERS        7
19:7.5 TANK TURNS.(HRS)  B34/B15
20:COST "A" COMP./GAL.   16
21:COST "C" COMP./GAL.   11
22:COST "B"OZ/GAL.       16
23:CONC.NI."C"OZ/GAL     40*.22
24:MAKEUP TANK GAL "C"   B9*.1
25:MAKEUP TANK GAL "A"   B24
26:DEIONIZED WATER GAL.  B9-(B24+B25)
27:COST FOR MAKEUP       (B24*B21)+(B25*B22)
28:ADD TANK GAL.  "C"    B9*.1
29:ADD TANK GAL.  "B"    B28
30:TOTAL ADDS "C"        B28*7
31:TOTAL ADDS "B"        B30
32:COST FOR ADDS         (B30*B21)+(B31*B22)
33:TOTAL COST 7 TURNS    B27+B32
34:OZ NI 7.5 TURNS       B30*B23+B24*B23/2
35:COST PER OP HOUR      B33/B19
36:
37:
38:LENGTH                       1.18              2.375             1.93              3.25
39:EN AREA                      6.13              12.51             13.13             22.46
40:PCS. PER RACK                220               110               110               64
41:YEARLY DEMAND                18768             9456              20952             8220
42:RACKS TO PLATE/YR.           C41/C40           D41/D40           E41/E40           F41/F40
43:HOURS TO PLATE               C42/B7/B8         D42/B8/B7         E42/B8/B7         F42/B8/B7
44:HOURS IN EN TANK             (C39*C41*B13)/B14 (D39*D41*B13)/B14 (E39*E41*B13)/B14 (F39*F41*B13)/B14
45:COST OF EN PER PART          B35*C44/C41       B35*D44/D41       B35*E44/E41       B35*F44/F41
46:
47:
48:                                               FIGURE 4.
```

HOIST PROGRAM RECORDING SET UP

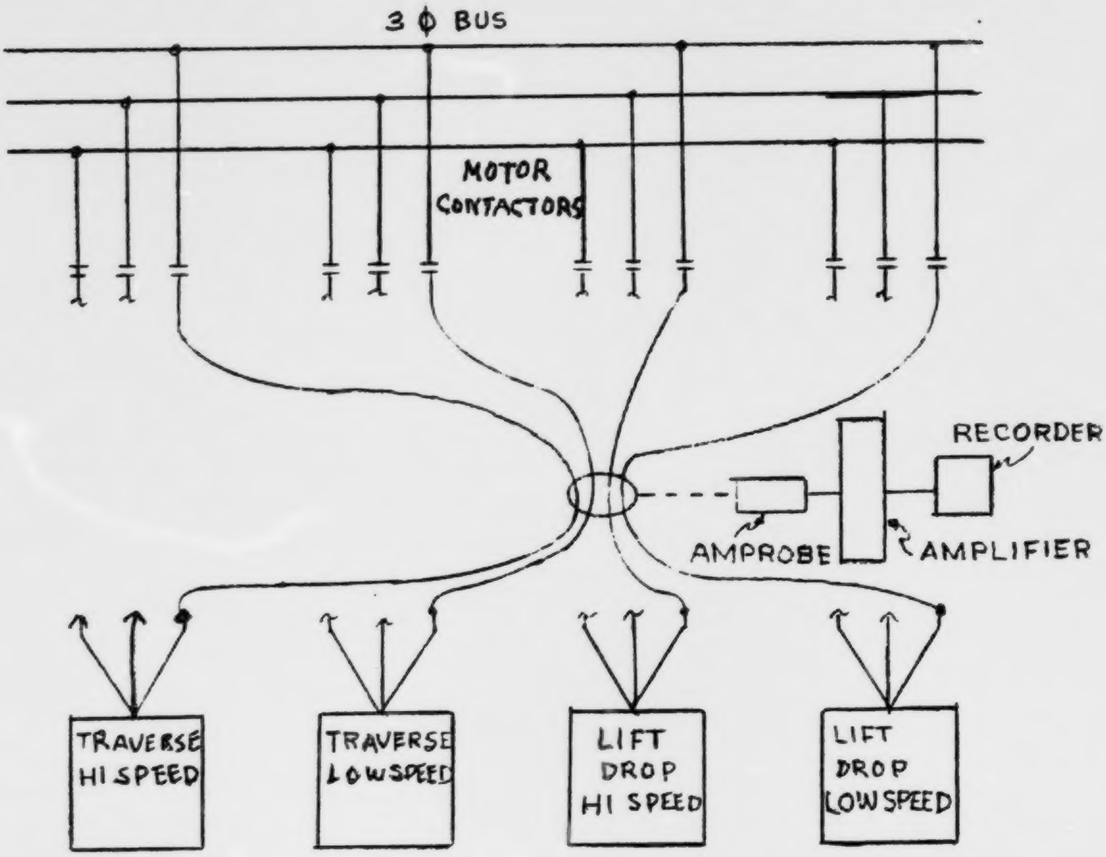
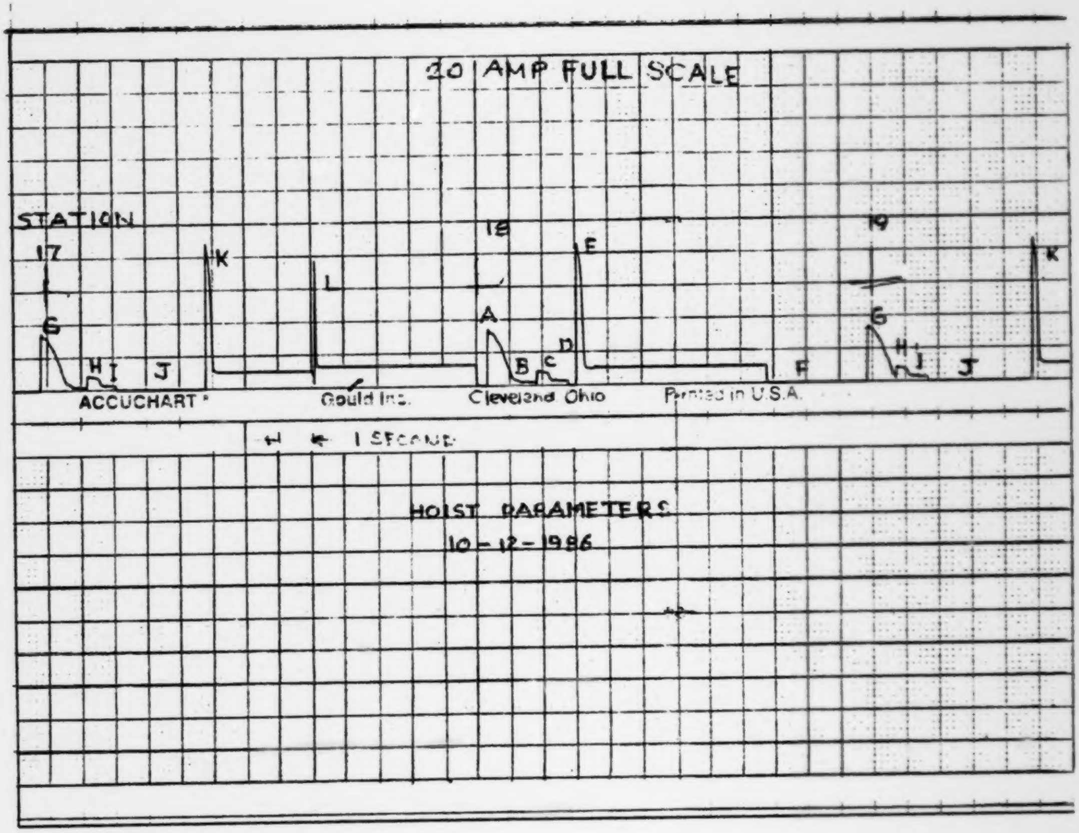

3 Φ BUS
MOTOR CONTACTORS
RECORDER
AMPROBE
AMPLIFIER
TRAVERSE HI SPEED
TRAVERSE LOW SPEED
LIFT DROP HI SPEED
LIFT DROP LOW SPEED

FIGURE 5


20 AMP FULL SCALE
STATION
17
18
19
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A
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F
G
H
I
J
K
ACCUCHART
Gould Inc.
Cleveland Ohio
Printed in U.S.A.
1 SECOND
HOIST PARAMETERS
10-12-1986

FIGURE 6

POLLUTION CONTROL USING ROOM TEMPERATURE EVAPORATORS

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ABSTRACT

The paper outlines how low energy room temperature evaporators have been added to five large automatic nickel-chrome plating machines to reclaim plating solutions and to reduce loads on a large chemical destruct system and lower the resulting metal hydroxide sludge. Details of rinse tank modifications to optimize the system are made. The effectiveness of the evaporative systems are an important step toward an eventual closed-loop system. Electrolytes include nickel, hex-chrome, and tri-chrome solutions.

Presented at the 8th AESP/EPA Pollution Control Conference February 9-11, 1987, San Diego, California.

Introduction

Although high temperature evaporators with vacuum capability have long been used to concentrate dragged-out plating solutions, they often require high capital investment, high energy consumption, and usually substantial maintenance attention. With certain high drag-out, high volume production situations they become even more impractical because of higher rinse volume requirements. With the pressure for constantly improving environmental results, every plating plant should be pushing toward some sort of closed-loop or near closed-loop system. Evaporators can be a major supplement to achieve these results.

The use of the evaporators without the need for temperature increases or vacuum input, combined with high corrosion resistance, results in low capital investment, very low energy consumption, and very little maintenance. The units can be sized and combined to total any number for practically any plating application and production volume. This paper will describe and detail the use of these room temperature evaporators at two different plating plants under heavy production conditions. The types of plating solutions being evaporated will include hexavalent chromium, trivalent chromium, and nickel. At Plant I, hexavalent chromium and nickel are being evaporated, and at Plant II, trivalent chromium and nickel.

Plant I

At this location approximately 1,800 different sized and designed parts are processed through three plating machines. The annualized totals are about 20,000,000 pieces and 10,000,000 square feet of nickel-chrome plated steel parts. About 80% of the total surface area plated involves tubular steel from simple straight lengths to highly complexed designs. Products represented include automotive, appliance, furniture, exercise equipment, food processing, store fixture, lawn equipment, and various other items. Some are simple to rinse, and some are extremely difficult.

The three machines involved include a single lane, split rail return type, approximately 105' long; a double lane, split rail return type 106' long; and a "U" shaped hoist line 28' wide by 115' long. The first machine contains 11,000 gallons of nickel solution and 2,000 gallons of hexavalent chromium. The second contains 11,000 gallons of nickel and 2,500 gallons of chromium; and the third contains 8,750 gallons of nickel and 3,500 gallons of chromium. All of the machines have been modified to include the exact same cleaning and rinse cycles.

Rinsing

All machines have five rinses between nickel and chromium and five rinses following the chromium. Four of the rinses after each plating tank counter-flow back through the evaporators and into the plating tank. The fifth and last rinse flows to a chemical destruct system to remove the remaining very small amounts of metallic ions. Spray nozzles are used at plating exit and drag-out rinses.

Evaporator Construction

With some small variations, the evaporators are constructed with the following materials and components:

- Housing - PVC, Polypropylene, or Polyethylene
- Evaporative Surface - Polypropylene Packing, random orientation
- Spray Nozzles - PVC Non-atomizing
- Mist Eliminator Baffles - PVC
- Access Doors
- Bottom Drain
- Air Outlet
- PVC Valves, Vinyl Hose, S.S. Clamps and Fittings
- Polypropylene or Kynar Pumps - Magnetic Drive, seal-less, 15 gpm @ 10 psi
- Dimensions: 72" long x 22" wide x 32" high

The evaporators operate on the following principles:

1. Evaporate from the plating tanks to provide more head room.
2. Evaporate from the drag-out tanks to concentrate rinse and return to the plating tank.
3. Evaporate from off-line heated 'bladder' tanks when necessary.

Principles of Operation

Unsaturated plant air will absorb moisture from wet surfaces. The higher the square feet of wet surface and the higher the volume of air, the more water will be evaporated. As the relative humidity drops, the rate of evaporation increases. Generally speaking, during the humid summer in Tennessee, the rate of evaporation drops somewhat and has to be taken into consideration when designing the system. Our approach is to add evaporative capacity to accomodate this season and to increase air flow. Hot nickel solution evaporates faster than warm chromium solution, so greater capacity has to be added to the chromium part of the system.

Individual Machine Units

The return-type machines each have four units on the chromium tanks and two on the nickel tanks. The hoist machine has three units on the chrome tanks and two on the nickel tanks. On the return-type chromium side, two units are used on the plating tanks to provide head room and two on the off-line bladder tank to concentrate the rinse water. This is necessary because the chrome operates at 110° F and requires more evaporation. The flow from the four drag-out tanks is diverted to the bladder tank for heating at 135° F. This is pumped to the evaporators and returned to the plating tank.

The nickel is operated at 140° F and assists in evaporation with about 300 square feet of plating tank surface area. The two evaporators on the nickels are used on the plating tanks to provide head room. The drag-out rinses are pumped directly into the plating tanks.

Results

During the past three operating years, no nickel salts have been purchased for these three machines, resulting in large savings in chemical cost. Due to the fact that nickel tanks slowly generate nickel salts in operation, the nickel content slowly rises. Total chromic acid consumption amounts to a few hundred pounds per month since there are no chrome anodes to replace what is plated out, or the small amount that is dragged out.

Plant II

This plant produces about 5,000,000 square feet of nickel-chrome plated surface annually, mostly in the form of stove tops and fabricated furniture. About 75% of the total are flat shapes amenable to spray rinsing.

Two hoist machines process the work through slightly longer plating cycles and utilize different rinse systems. One machine has two trivalent chrome tanks, and the second machine a single trivalent tank.

Rinsing

Four rinses are used after the nickel and five after the chrome. The first two after the nickel are counter-pumped back into the nickel tanks which employ two evaporators to provide head room. The second two are counter-flowed, and the effluent goes to the city sewer.

The first trivalent chrome rinse is spray only using the second rinse as the water source. Since the concentration of chrome metal in the trivalent tank is approximately one-seventh the concentration of a typical hexavalent solution, the last three chrome rinses are counter-flowed to the sewer.

Evaporation

The large amount of surface area of the nickel tanks operating at 140° F provides significant head room, and again, needs less assistance from the evaporators.

The trivalent chrome operates at 65°-75° F and results in very little evaporative effect. Four room temperature evaporators are used on one line and two on the second line. During the summer months, the effect of humid air on the evaporation rates are much more dramatic on the trivalent system due to an average operating temperature of about 40° F less than the hexavalent chrome system. All things being equal, the trivalent chrome will require significantly more evaporative capacity than will the hexavalent.

Waste Treatment

All Plant II final rinses flow to the sewer and are continuously monitored by the city for compliance with POTW numbers. There is no need for a chemical destruct system. The total treatment system comprises only counter-flow rinses, sprays, and evaporators.

Summary

The room temperature evaporators offer significant advantages over high temperature-vacuum evaporators in the two plants described here. Much lower capital investment, lower operating costs, lower maintenance costs, and high reliability are the primary factors justifying their use.

Evaporators in general save dramatically on chemical costs, and the investment payback on the room temperature evaporators is much faster than the high temperature units. Often the entire system can offer a payback in a matter of months.

The ultimate effect on EPA compliance numbers is equally dramatic. Even though POTW numbers generally allow several parts per million of metallics in the effluent stream, Plant I averages about one-tenth the allowable limits. Plant II averages about one-fourth to one-half the mandated limits.

Each production plant contemplating the use of room temperature evaporators will have to design its own system based on its own production realities. There are several manufacturers of these units, and their technical sales staff will be able to offer valuable assistance to accomplish the objectives.

HOWARD PLATING CLEANS UP THEIR ACT WITH MAGNESIUM HYDROXIDE

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INTRODUCTION

Howard Plating Industries is located in the metropolitan Detroit suburb of Madison Heights. We provide metal finishing services for the automotive industry and employ nearly 250 full time workers. Our facility operates 24 hours per day and occupies 150,000 square feet. Howard Plating Industries provides zinc electroplating, chrome dip, zinc phosphate and water-based electropainting finishes.

The total waste water effluent from the metal finishing processes amounts to 0.4 million gallons per day. Significant concentration of dissolved zinc, iron and chromium and minor concentrations of nickel, copper, lead, manganese and cadmium are present. (Table 1). These waste waters are neutralized with magnesium hydroxide and caustic soda in order to precipitate the dissolved metals, as hydroxides, for eventual collection in a plate and frame filter press. Introduction of magnesium hydroxide has markedly increased sludge particle density, improved filterability and produced better water quality at our plant.

TABLE 1

HOWARD PLATING INDUSTRIES
WASTE WATER CHARACTERIZATION
(UNTREATED)

SAMPLE #	Zn	Fe	Cr	Ni	Cu	Pb	Mn	Cd
1	1073	652	105	5.6	0.9	1.1	3.6	0.3
2	1495	972	177	5.0	1.7	6.5	3.8	0.9
3	1645	1069	97	5.7	1.1	1.1	4.8	0.3

METAL RESULTS WERE OBTAINED FOLLOWING TOTAL DIGESTION OF UNFILTERED WASTE WATER WITH ACID.

PLANT LAYOUT

Waste waters are collected by gravity flow into three main sumps and pumped to treatment tanks where the appropriate chemicals are combined with the waste water. Rinse waters from the electro and soak cleaning, pickling and plating processes are collected in the acid/alkali (A/A) sump having a usable capacity of 30,000 gallons. Magnesium hydroxide is added into this sump in order to take advantage of the available mixing and residence time. Hexavalent chromate waste water is contained in a 5000 gallon sump. Waste acid is pumped into totes and subsequently consumed for pH adjustment and chromate treatment. Concentrated spent cleaning solutions are collected in the concentrate sump and metered slowly into the A/A sump to achieve equalization.

The first treatment tank in the flow through system is utilized to perform hexavalent chromate reduction to trivalent chrome. This process is achieved by the addition of sodium metabisulfite at a pH between 2.0 and 2.5. The effluent from this treatment tank flows into the first neutralization tank (NI).

In NI, the addition of waste acid or liquid caustic maintains the pH within the desired range of 7.5 to 9.5. The lower pH setting is deliberately designed to allow more mixing and greater residence time for the waste water and magnesium hydroxide reaction to occur before addition of liquid caustic.

The pH is finally adjusted to between 8.5 and 9.5 with caustic in the second neutralization tank (NII). The volume of each of these neutralization tanks is 3500 gallons. At a flow rate of 350 gallons per minute, each neutralization treatment tank allows 10 minutes retention time.

The treated waste water is then mixed with an anionic polymer emulsion at the rate of 10 ppm to promote flocculation. Clarification through two parallel flow slant plate lamella gravity clarifiers and thickening of the sludge follows. Clarified water is discharged to sewer.

The dewatering of the sludge is achieved with a 25 cubic foot plate and frame filter press. The filtering pressure is gradually increased to and maintained at 95 psi for 4 to 8 hours with an air operated diaphragm pump to produce a hard filter cake. The solid filter cake obtained by using magnesium hydroxide is easily removed from the filter cloths and collected for disposal.

THE PROBLEM

Prior to the introduction of magnesium hydroxide into the waste water treatment sytem, frequent deficiencies were experienced. Suspended solids were routinely carried out along with overflowing clarified water and consequently were discharged. Filter press cakes were consistently soft and occasionally flowable. Average solids content of the filter cakes was 24.6% and ranged between 15% and 30% when neutralization was achieved by sodium hydroxide alone. The sodium hydroxide sludge, being difficult to dewater, also necessitated frequent time consuming maintenance and repair of the filter press and sludge handling system.

Poor water quality resulted from these combined problems.

LAB TRIAL

A laboratory trial was performed in which waste water from our plant was neutralized with sodium hydroxide, magnesium hydroxide and both sodium hydroxide and mangesium hydroxide. The samples were neutralized to various pH's.

It was observed that the removal of metals was sufficient as long as the pH was 7.5 or higher. (Table 2). Magnesium hydroxide alone required 37 minutes to reach the desired pH. A combination of magnesium hydroxide and sodium hydroxide required 25 minutes of residence time.

Sludge settling rates were dramatically improved by the addition of magnesium hydroxide even in combination with sodium hydroxide. The sludge, formed by an alkali ratio of 90% magnesium hydroxide and 10% sodium hydroxide, settled in 10 minutes. Sludge formed by caustic alone required 90 minutes to settle.

The lab trial indicated that zinc, chromium and other metals in the waste stream could be effectively removed by using magnesium hydroxide. The sludge volume would be reduced by 60% and the settling time reduced by 88% compared to caustic soda alone.

TABLE 2

HOWARD PLATING INDUSTRIES
LABORATORY TRIAL RESULTS

Sample	Base	pH	Neutralization Time (min)	Zn	Cr	Cu	Ni	Floc Settling Volume/Time
1	1.75 meq NaOH	9.1	—	0.16	0	<0.1	0	20 ml/3 min 18 ml/12 min 15 ml/2 hrs
2	1.40 meq NaOH	6.0	—	104	0	<0.1	0	12ml/2 min 8 ml/90 min
3	Untreated	1.4	—	124	7.8	<0.1	0.3	—
4	1.79 meq NaOH	9.9	—	0.14	0	<0.1	0	15 ml/90 min
5	1.75 meq $Mg(OH)_2$	7.9	37	1.02	0	<0.1	0	1 ml/1 min
6	1.40 meq $Mg(OH)_2$	10.4	1	0.04	0	<0.1	0	~45 ml/1 min 35 ml/7 min 30 ml/100 min
7	1.40 meq $Mg(OH)_2$ 0.39 meq NaOH	7.4	25	1.06	0	<0.1	0	11 ml/2 min 8 ml/90 min
8	1.75 meq $Mg(OH)_2$ 0.175 meq NaOH	7.5	25	0.68	0	<0.1	0	8 ml/1 min 6 ml/10 min

TABLE PREPARED BY DOW CHEMICAL U.S.A., SPECIALTY CHEMICALS DEPARTMENT, MIDLAND, MI 48640

PLANT TRIAL

The positive laboratory results prompted us to conduct a plant trial. The addition rate of magnesium hydroxide was adjusted during the trial to determine the optimum quantity, with repsect to the metal removal efficiency, sludge density, and settling rate.

Minimally acceptable water quality was achieved when the pH was maintained above 7.5 as was indicated by the lab trial. The upper limit automatically became the pH of 9.5 at which magnesium hydroxide begins to precipitate from solution.

The solids content of the sludge removed from the filter press ranged from 27% to 50%. The measured sludge densities gradually increased during the course of the trial.

Another observed benefit was the reduction in the amount of anionic polymer required for flocculation. At times, a very pronounced floc formation was even observed in the second neutralization tank before polymer addition.

An unexpected high usage of caustic soda was observed during the plant trial. Caustic usage was found to be only slightly decreased while the recommended amount of mangesium hydroxide was added. It was concluded that both mixing and residence time were inadequate. The design of our flow-through system was based upon the fast neutralization reaction available from liquid caustic. As a result, we added the magnesium hydroxide to our waste stream at a point into a trough well upstream of the holding sump and repositioned the outfall into the A/A sump to maximize retention and mixing time.

EQUIPMENT NEEDED

Storage of magnesium hydroxide presents some special problems. The slurry will settle upon standing. The longer the solids are allowed to accumulate, the more difficult they become to resuspend. Vibration and dilution of the original slurry accelerates settling rates. Therefore, the storage tank must be designed to accomodate a mixer. It is suggested that the storage tank have a capacity of 1.5 times the volume of a tank truck shipment plus rinse water for unloading. Vertical, cylindrical tanks with a 1:1 to 1:2 diameter to height ratio are more easily supported on concrete slabs and are more easily agitated. Storage tanks made of carbon steel are preferable because they offer better support to a top mounted mixer. A coal tar epoxy coating eliminates corrosion which should be less than 5 mpy for steel.

Magnesium hydroxide slurry is unique because it does not behave like an ideal fluid. The viscosity of the slurry (4-40 poise) decreases with increased shear rates and decreased solids content. The liquid also tends to resist flow until a certain pressure (yield point) is reached.

Placement of the storage tank should take into account the viscosity of the slurry. Minimized pumping distances will reduce equipment and operating costs. Tanks which are exposed to temperatures below 40°F will require insulation and heating to prevent freezing or an increase in viscosity.

Another important aspect to consider is the requirement for slurry agitation. Adequate agitation can be provided with a top mounted pitch blade turbine mixer. General specifications for turbine agitators include 0.5 horsepower per 1000 gallons, 1.25 gearing factor of safety, splash and dip oiling, deep well seal, change gears and helical and spiral bevel gearing. Agitation of 1/2 hour out of four hours total time is sufficient to maintain slurry suspension.

The pumping requirements for magnesium hydroxide favor centrifugal and positive displacement pumps. Centrifugal pumps with hardened steel shafts and carbon steel housings are commonly used for transferring large volumes. Progressive cavity pumps having a cast iron housing, hardened steel rotor and Buna N stator are used for delivering a particular flow rate or higher pressures.

In our particular situation, we found that a peristaltic tube pump was superior for delivering a controlled flow rate. This pump with a variable speed drive is linked to a pH controller located over the A/A rinse sump. At a pH of 8, the pump will deliver a minimum flow rate of less than 3 gallons per hour. As the pH decreases, the flow rate will increase accordingly. The variable speed drive motor responds to a reversed 4-20 mA signal produced by the pH controller.

ECONOMICS

Initially we experienced a higher usage rate than expected for both magnesium hydroxide and liquid caustic as mentioned earlier. Changes were made to improve mixing and residence time. More efficient usage of both reagents resulted. Further fine tuning of the addition rate of magnesium hydroxide over the next three months revealed that decreasing the amount of magnesium hydroxide usage only slightly increased liquid caustic usage.

The average liquid caustic usage per month prior to implementing neutralization with magnesium hydroxide was 8159 gallons. (Table 3). The usage of caustic dropped to 4176 gallons with the addition of 3607 gallons of magnesium hydroxide slurry. A cost comparison over this entire period indicates a slight increase. However, if we consider the three month period from June through August during which we reduced the magnesium hydroxide to its lowest consumption rates, a better economic outlook is apparent. The average consumptions for caustic and magnesium hydroxide were 4155 gallons and 2872 gallons, respectively. This reduction in alkali consumption represents a 9% cost savings.

TABLE 3

HOWARD PLATING INDUSTRIES
CHEMICAL CONSUMPTION

	JUNE	JULY	AUGUST	AVG.	1985 AVG.
CAUSTIC USED (GAL)	4680	3430	4355	4155	8159
$Mg(OH)_2$ USED (GAL)	3909	2720	1986	2872	

Although the amount of liquid anionic polymer emulsion consumed remained constant with the addition of magnesium hydroxide, it became possible to use a less expensive polymer without diminishing water quality. The cost per gallon of the polymer required when using liquid caustic alone was $16.90/gal. The less expensive polymer used with magnesium hydroxide costs $10.75/gal. This represents a reduction in polymer costs of 36%. Another

Another added benefit is the reduction of sulfuric acid usage. When neutralizing with liquid caustic alone, there is a great tendency to over shoot the upper pH limit, thus requiring the addition of acid to lower the pH below 9.5. Because of the buffering effect of magnesium hydroxide at a pH of 9.0, there is not that tendency to surpass the upper pH limit. We have been able to satisfy our acid requirement by using our waste pickle liquor alone. Thereby, we have saved 800 gallons of raw acid per month.

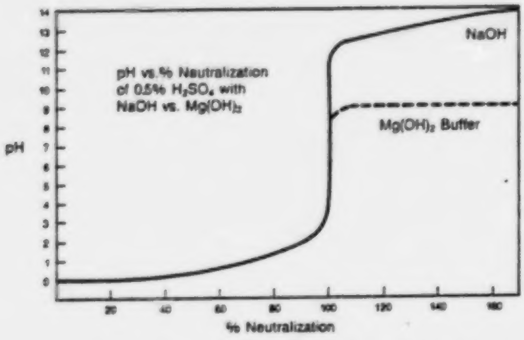
ADVANTAGES

There are several distinct advantages when using magnesium hydroxide as a neutralizing reagent. The economic advantage of reduced chemical consumption has been discussed. There are also economic advantages related to reduced waste disposal costs, reduced possibility of receiving fines and penalties for unacceptable waste water discharges, and lower operating and maintenance costs for the filtering system.

The buffering effect of magnesium hydroxide at a pH of 9.0 is also an advantage. Overtreatment with liquid caustic can result in discharges of waste water with a pH as high as 14. This type of discharge exceeds federal limits of the Clean Water Act, redissolves metals, and is hazardous to human health and the environment.

If overtreatment with magnesium hydroxide occurs, the pH of the effluent would be no higher than 9. (Figure 1). This pH is within acceptable limits and does not pose severe detrimental effects on the environment.

FIGURE 1



At 100% neutralization of a 0.5% solution of sulfuric acid, the pH rises steeply, making overtreatment to a level as high as 14 difficult to avoid when using caustic soda. Note, however, that $Mg(OH)_2$ peaks at a pH of 9, a far more acceptable level.

Safety is a major concern when dealing with caustic soda. Extreme care must be taken to avoid contact with the eyes and skin. Mists are damaging to throat and lungs. Severe and permanent damage to health can result from accidental exposures to caustic soda.

Magnesium hydroxide poses little threat to human health. Ingestion can cause diarrhea and cramps. Contact with the eye can cause moderate irritation or temporary injury. Skin contact is usually not a problem.

Handling of liquid caustic poses a problem becasue of the corrosivity of the product. Special pump construction and design is necessary. Extreme care for personal health and safety must be exercised. Freezing of the 50% solution occurs at 57°F which can present difficulties.

On the other hand, magnesium hydroxide requires no special pumping equipment or safety procedures. Freezing of the slurry is not a special problem since the freezing point is the same as water.

One of the most important advantages is the affect magnesium hydroxide exhibits on sludge density. Significatnly increased settling rates were observed when using magnesium hydroxide. Jar test samples that would normally settle to one half their volume in 30 seconds with sodium hydroxide alone would only require 10 seconds when a portion of the alkali was replaced with magnesium hydroxide.

An increase in the solids content of the filter press cake also was observed. With liquid caustic neutralization alone, the average solids content was 23%. (Table 4). When using a combination of sodium hydroxide and magnesium hydroxide, the average solids increased to 39%. The increased filterability (porosity and permeability), due to the particulate nature of the sludge, facilitates the production of a denser cake and a reduced amount of sludge. Therefore, a significant reduction in sludge disposal costs can be realized.

TABLE 4

FILTER CAKE PER CENT SOLIDS

BEFORE ADDING $Mg(OH)_2$		AFTER ADDING $Mg(OH)_2$	
May 13, 1985	20.3	Mar 19, 1985	34.4
May 17, 1985	13.8	Apr 2, 1985	34.4
Jun 4, 1985	29.1	Apr 7, 1985	47.8
Jun 26, 1985	19.8	Apr 12, 1985	46.8
Aug 28, 1985	27.0	Apr 29, 1985	32.9
Sep 13, 1985	28.5	May 9, 1985	45.9
Sep 28, 1985	29.2	Jun 4, 1985	27.4
Sep 28, 1985	25.0	Jun 14, 1985	46.4
Oct 5, 1985	15.3	Jun 19, 1985	39.3
		Jun 25, 1985	27.1
		Aug 26, 1985	28.4
		Sep 12, 1985	41.3
AVERAGE 23.1		AVERAGE 39.0	

Improved water quality can be achieved using magnesium hydroxide. As long as the pH remains above 7.5, metals are effectively removed from the waste stream. (Table 5). The removal of metals at a lower pH than that experienced with liquid caustic alone is caused by the phenomenon of surface absorption. Not only does magnesium hydroxide provide hydroxyl ions for metal removal, but it also absorbs metal ions onto its surface.

TABLE 5

HOWARD PLATING INDUSTRIES
TREATED WASTE WATER TREATMENT

SAMPLE #	ph	Zn	Fe	Cr	Ni	Cu	Pb	Mn	Cd
1	8.8	0.5	ND	ND	ND	0.05	ND	0.1	ND
2	8.3	4.0	ND	ND	0.2	ND	ND	0.5	ND
3	8.1	1.0	ND	ND	0.1	ND	ND	0.6	ND

DIFFICULTIES ENCOUNTERED

The implementation of magensium hydroxide presented some difficulties. One of the problems encountered was clogged piping. The slurry exhibits a marked tendency to settle out in pipes if not kept moving. With the pump continuously running, little or no problem with plugging of pipes exists. However, during long periods of shutdown, settling occurs causing clogged pipes. It became necessary to reroute the slurry feed from the storage tank to the waste water stream so that the delivery point was much closer to the tank. We also installed an inline water feed to help flush out the line and prevent the accumulation of solids.

The shortcoming of our choice of pumps also soon presented itself. We had chosen a rotor and stator type positive displacement pump. It soon became apparent that this design was not suitable for delivering small volumes accurately. Variations in the slurry level in the storage tank had a tremendous effect on the delivery rate of the pump. Product was forced through the pump even when the pump was not running. This problem could not be compensated for by the variable speed controller. This situation was rectified by substituting a peristaltic tube pump for the original pump.

Because of the flow through nature of our waste water treatment system, it is not possible to measure the precise amount of magnesium hydroxide necessary and deliver that amount properly as suggested for batch treatment operations. Therefore, once the system is in operation, it is necessary to fine tune the system by adjusting the target pH to achieve the most economical and efficient usage of magnesium hydroxide.

The single most difficult problem we encountered in incorporating magnesium hydroxide was the lack of sufficient residence time available in our system. Several options were considered:

1. Incorporate additional waste water treatment tank capacity.
2. Prevent shortcircuiting in available treatment tanks.
3. Increase agitation.
4. Introduce magnesium hydroxide upstream from treatment tanks.
5. Add liquid caustic to top off just prior to flocculation.

SUMMARY

The addition of magnesium hydroxide to the waste water treatment process has demonstrated the benefits of reduced chemical consumption, improved sludge handling, reduced maintenance requirements, and improved water quality. The use of magnesium hydroxide is highly recommended for batch treatment systems. Although the efficient use of this product in a continuous flow system may be more difficult to achieve, its usage should be investigated as an alternative to other alkali sources because of these significant benefits.

METAL FINISHING WASTEWATER TREATMENT UPGRADE WITH AN INSOLUBLE SULFIDE PRECIPITATION PROCESS

Ronald V. Bazza, Christine M. Kelleher, M.B. Yeligar*

INTRODUCTION

A large manufacturing complex owned by Texas Instruments Incorporated (TI) in Attleboro, Massachusetts is involved in the semiconductor packaging, metal finishing and metal forming operations for a diversified product line. These manufacturing operations generate numerous wastewater streams which require treatment prior to discharge.

Recently, the Attleboro facility received a new National Pollutant Discharge Elimination System (NPDES) Permit for surface water discharges. Because wastes are discharged to a stream with high quality, the new effluent limitations for the primary industrial waste stream, as dictated by the Amendments of 1977 to the Clean Water Act, are among the most stringent in the country. Additionally, the City of Attleboro received an NPDES Permit with similar limitations for its sewage treatment plant to which Texas Instruments directs a secondary industrial waste stream. New pretreatment standards for this stream reflect the Attleboro limits.

In order to comply with the new NPDES Permit limitations and the anticipated pretreatment standards for discharges to the city sanitary sewer, Texas Instruments retained United Engineers & Constructors for the design of the required industrial wastewater treatment system upgrade. The scope of work for the project included a comprehensive source reduction study, pilot testing of state-of-the-art treatment technologies, and design implementation of these technologies and processes to polish the effluents prior to discharge. The project also required the design of modifications to the existing wastewater treatment systems and design of a new building addition to house the advanced treatment polishing systems.

The advanced technologies which underwent comprehensive pilot testing included membrane microfiltration, chelating resin ion exchange, a soluble sulfide precipitation process, and an insoluble sulfide precipitation process (SULFEX^TN)[1]. Although each of the technologies showed encouraging results, the overall evaluation for this specific application favored selection of the insoluble sulfide precipitation process which is the focus of this report.

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BACKGROUND

DISCHARGE PERMIT REQUIREMENTS

In July 1977, Texas Instruments received a five-year National Pollutant Discharge Elimination System (NPDES) permit to discharge treated industrial wastewater to an on-site ten acre surface water body, Coopers Pond. TI had just completed the installation of a modern 600 gallon per minute waste treatment facility employing metal hydroxide precipitation. At the time, this system was considered to meet Best Available Technology (BAT) requirements, and it was based on such process chemistry criteria that the original permit limits were generated.

In 1982, however, when TI submitted a renewal application for its NPDES Permit, water quality criteria of the receiving stream in lieu of BAT was used by the U.S. Environmental Protection Agency to develop the new permit limits. This resulted in the imposition of very stringent effluent limitations in the new draft permit. Due to the limited dilution water available in TI's receiving stream, the proposed limits were deemed impossible to meet with any existing technology.

TI then faced a difficult decision on whether to attempt to seek relief from the non-attainable proposed limits through aquatic toxicity testing, or whether to re-direct the effluent to another receiving stream (i.e., the Publicly Owned Treatment Works). In the worst case, TI had to decide whether to shut-down its large Attleboro based manufacturing facility employing over 5,000 people and relocate to another area.

In the final analysis and after much deliberation, TI chose to maintain its Attleboro facility and enter into a long and relatively unexplored avenue of aquatic toxicity testing to raise its permit limits to achievable levels. It was realized early on, that, even if TI succeeded in raising the limits, the existing waste treatment facility would require substantial modifications.

The Commonwealth of Massachusetts and the U.S. EPA are currently using site-specific water quality criteria in evaluating effects of direct discharges. These criteria are designed to evaluate effects of a discharge on representative, sensitive species plus indigenous populations and allow for establishing discharge limits which will protect aquatic environments. Data to support this program and establish acceptable in-stream limits are derived from a series of bioassays utilizing selected species exposed to effluent samples and site specific dilution water. When these studies indicate that a discharge has potential for adverse environmental impact, a toxicity reduction evaluation is conducted to determine the source of toxicity in the effluent and the means to reduce this source.

Early toxicity testing of TI's conventionally treated effluent determined that, in order to reduce toxicity, trace metals in the discharge would have to be reduced significantly. Through these tests, the U.S. EPA established in the draft permit the concentration of effluent trace metals which it believed would achieve the desired water quality in Coopers Pond.

To reach the goal of no toxic materials in toxic amounts, TI elected to evaluate advanced treatment technologies to determine if acceptable effluent quality could be attained. During this pilot testing program, a series of acute and chronic toxicity tests were conducted using treated effluent from the pilot units. The toxicity data generated during this period was evaluated and used by the U.S. EPA to establish somewhat less stringent limits in TI's final NPDES permit. Table I presents a comparison of the draft effluent limitations with those imposed by the final permit.

TABLE I

NPDES PERMIT LIMITS (mg/l)

Parameter	Draft Permit Monthly Avg.	Draft Permit Daily Max.	Final Permit Monthly Avg.	Final Permit Daily Max.
Oil & Grease	15	15	15	15
TSS	20	30	20	30
Nickel	0.15	2.0	0.17	2.0
Iron	1.75	1.75	1.75	1.75
Aluminum	0.04	0.5	1.0	1.25
Copper	0.15	0.15	0.15	0.15
Zinc	0.5	0.75	0.4	0.75
Cadmium	0.025	0.025	0.025	0.025
Silver	0.008	0.035	0.007	0.05
Chromium(+3)	0.12	1.5	0.1	1.5
Chromium(+6)	0.01	0.02	0.09	0.09
Lead	0.01	0.15	0.031	0.15
Tin	0.01	0.08	0.02	0.08
Ammonia	1.6	4.1	1.7	4.1
Residual Chlorine	0.025	0.025	0.02	0.025
Selenium	0.1	0.45	0.1	0.45
Cyanide	0.015	0.04	0.13	0.185
Fluoride	2.6	2.6	9.0	9.1
Phosphorus	1.0	1.3	1.0	1.0
Palladium	1.05	1.1	1.05	1.1
Boron	0.015	0.02	2.0	2.0
Total Toxic Organics	-	2.13	-	2.13
NOAEL	-	60%	-	60%
NOCEL	-	-	-	Monitor Only

PILOT TESTING

In order to establish baseline toxicity, design and operating data for the advanced treatment processes required to meet TI's new permit limits, a comprehensive pilot testing program was developed. Selected state-of-the-art technologies which were tested included the following:

- Insoluble (iron) sulfide precipitation process.

- Membrane microfiltration.
- Chelating resin ion exchange.
- Soluble (sodium) sulfide precipitation and filtration.

The testing program required several months of data collection, from June through October, 1985. As noted previously, effluent samples from each pilot unit were subjected to biotoxicity testing in addition to analyses for the constituents listed in the new discharge permit. This in-depth testing, data collection and data analyses eventually determined:

- The feasibility of advanced treatment to produce an effluent meeting the new U.S. EPA discharge criteria.
- Estimations of full-scale chemical consumption rates and chemical costs.
- Operational and maintenance advantages and disadvantages of each process.
- Process turndown capabilities and operational flexibility.
- Full-scale design parameters.

For this specific project, the pilot testing favored the selection of the insoluble sulfide precipitation process for advanced treatment and polishing of TI's effluent from the existing hydroxide precipitation treatment system.

INSOLUBLE SULFIDE PRECIPITATION

PROCESS CHEMISTRY DESCRIPTION

The insoluble sulfide precipitation process is a wastewater treatment technology which has been proven effective in separating heavy metals from plating and metal finishing wastewaters. The process uses a freshly prepared ferrous sulfide (FeS) slurry as the source of the sulfide ions needed to precipitate the metals from the wastewater. The process operates on the prinicple that FeS will dissociate into ferrous ions and sulfide ions to the degree predicted by its solubility product. As sulfide ions are consumed by forming precipitates with metal ions in the wastewater, additional FeS will dissociate to maintain an equilibrium concentration. Ferrous ions dissociated from the FeS will precipitate as ferrous hydroxide at the alkaline pH (8 to 9 standard units) at which the process is operated. The sulfide precipitation process can produce an effluent having much lower dissolved metals than a hydroxide precipitation process because metal sulfides are much less soluble than metal hydroxides. Table II compares the solubilities of metal sulfides with hydroxides to illustrate this phenomena. Figure I shows the theoretical or calculated solubilities of various examples of these heavy metals as a function of pH value. The insoluble sulfide precipitation process removes only those metal ions which can form metal sulfides having lower solubility than the ferrous sulfide. For example, the process will not be effective for removal of manganese (Mn) because MnS is more soluble than FeS. The process will also not remove cyanides and other anions. Hexavalent chrome will be reduced to trivalent chrome and then removed by forming hydroxide precipitates according to the following reaction:

$$CrO_4^{=} + FeS + 4H_2O \longrightarrow Fe(OH)_3 + Cr(OH)_3 + S + 2\,OH^{=}$$

The process can be effective in removing dissolved metals from wastewaters containing certain common chelating agents and complex organics such as ammonium, succinates, gluconates, pyrophosphates, tartrates, Rochelle salts and EDTA. The degree of metal removal depends upon the specific chelating complex as well as the specific metal ion present in the wastewater. For example, the reaction with copper (Cu) ions in a solution containing EDTA can be predicted as follows:

$$Cu\ EDTA^{-2} + FeS \longrightarrow CuS + Fe\ EDTA^{-2}$$

The reaction will proceed to the right because CuS is less soluble than FeS and Fe $EDTA^{-2}$ is more stable than the Cu $EDTA^{-2}$ complex.

To control the excess iron in the system, the process is maintained at a pH in the range of 8.5 to 9.0 forming an iron hydroxide precipitate with the excess Fe ions. Within this pH range, there is no significant discharge of soluble sulfide or iron sulfide in the effluent to cause generation of hydrogen sulfide gas (H_2S). Routine operation of the process requires that excess ferrous sulfide be maintained in the reactor to accommodate any sudden increases in the concentrations of metal ions in the influent.

TABLE II

THEORETICAL SOLUBILITIES OF HYDROXIDES AND SULFIDES OF HEAVY METALS IN PURE WATER

Metal	Solubility of Metal Ion (mg/l)	
	As Hydroxide	As Sulfide
Cadmium (Cd^{++})	2.3×10^{-5}	6.7×10^{-10}
Chromium (Cr^{+++})	*8.4×10^{-4}	No Precip.
Cobalt (Co^{++})	*2.2×10^{-1}	1.0×10^{-8}
Copper (Cu^{++})	**2.2×10^{-2}	5.8×10^{-18}
Iron (Fe^{++})	8.9×10^{-1}	3.4×10^{-5}
Lead (Pb^{++})	**2.1	3.8×10^{-9}
Manganese (Mn^{++})	1.2	2.1×10^{-3}
Mercury (Hg^{++})	*3.9×10^{-4}	9.0×10^{-20}
Nickel (Ni^{++})	*6.9×10^{-3}	6.9×10^{-8}
Silver (Ag^{+})	13.3	7.4×10^{-12}
Tin (Sn^{++})	**1.1×10^{-4}	*3.8×10^{-8}
Zinc (Zn^{++})	1.1	2.3×10^{-7}

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The Chemical Rubber Co., 1969, p. B252

*Handbook of Analytical Chemistry, L. Meites, Ed.
McGraw-Hill Inc., 1963, p.p. 1-15 to 1-19

**Ionic Equilibrium As Applied to Qualitative Analysis.
Hogness and Johnson, Holt, and Winston Co., 1954, p.p. 360 - 362

THEORETICAL SOLUBILITIES OF METAL HYDROXIDES AND SULFIDES AS A FUNCTION OF pH

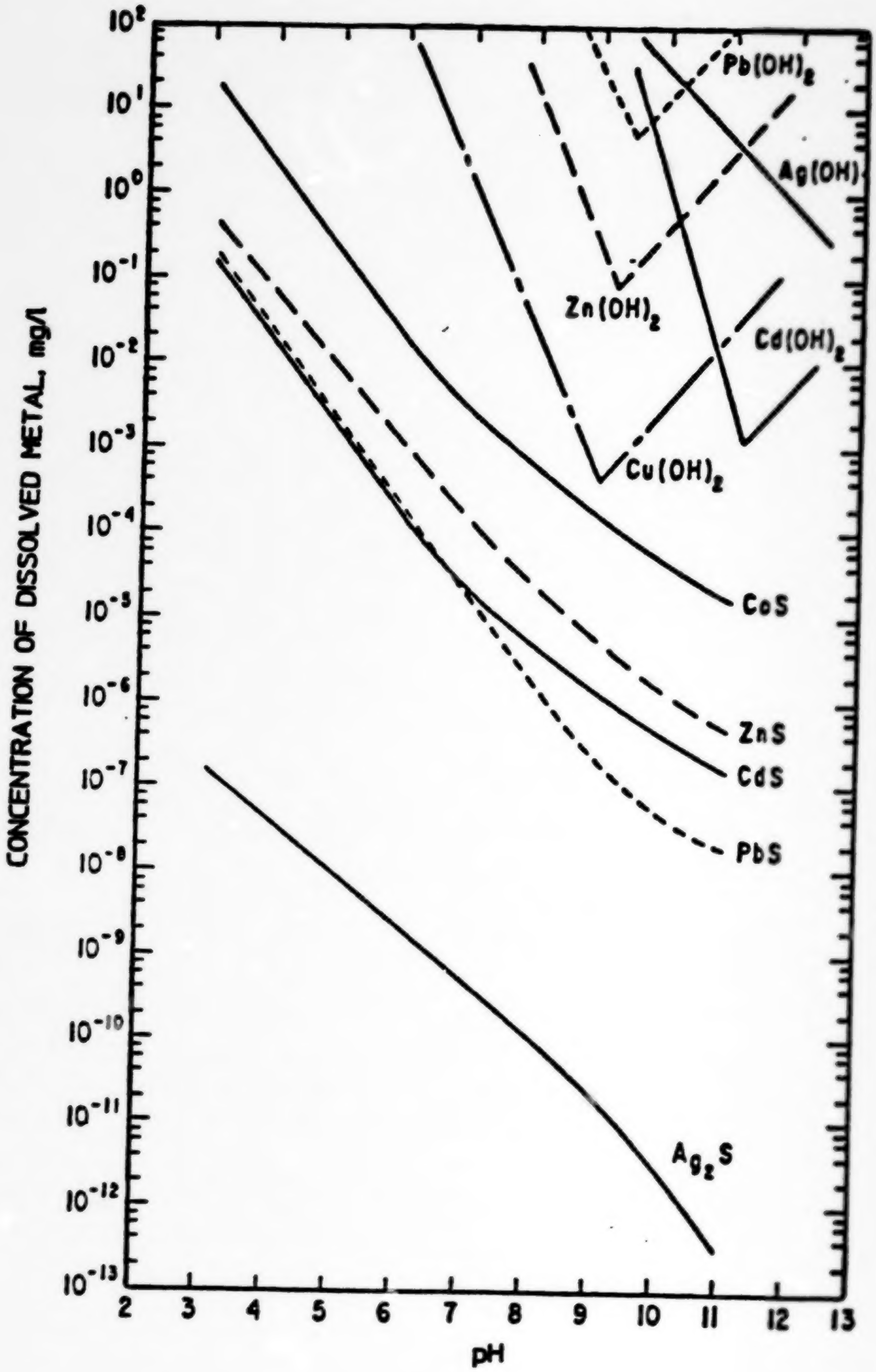


FIGURE I

In the reactor, the FeS slurry dissolves to react with many other metal contaminants in the wastewater according to the following reactions (where Me = metal ion):

$$FeS \longrightarrow Fe^{++} + S^{=}$$

$$Me(OH)_2 \longrightarrow Me^{++} + 2\,(OH)^{-}$$

$$Me^{++} + S^{=} \longrightarrow MeS$$

$$Fe^{++} + 2(OH)^{-} \longrightarrow Fe(OH)_2$$

The overall chemistry of the process for metal (Me) removal may be illustrated by the following equation:

$$Me\,(OH)_2 + FeS \longrightarrow Fe\,(OH)_2 + MeS$$

According to the above reactions, ferrous sulfide in the sludge blanket is gradually converted to ferrous hydroxide sludge. The increase of ferrous hydroxide in the sludge can impair the solubility of ferrous sulfide, thus limiting the available sulfide for metal precipitation. This occurs because $Fe(OH)_2$ is more soluble than FeS. High concentrations of ferrous ions in equilibrium with $Fe(OH)_2$ must be controlled through periodic blowdown of the mixed sludge in the reactor. Makeup of freshly prepared ferrous sulfide must be added to replenish that consumed by reaction conversion and sludge blowdown operations.

Economical operation of the insoluble sulfide precipitation process requires proper control of ferrous sulfide addition and sludge blowdown to minimize excess sulfide loss.

PILOT PLANT DESCRIPTION

The pilot plant for the process was delivered to the TI's Attleboro plant in mid-May, 1985. Following approximately two weeks of mechanical setup and process chemistry tuning, the pilot unit was set to operate on waste streams from TI's existing wastewater treatment facility.

The pilot plant consisted of three major components: a sludge blanket precipitator[2], a dual media filter, and a chemical feed system. The sludge blanket precipitator was separately skid-mounted with all other equipment mounted on a flat-bed trailer. Figure II presents a process flow schematic of the insoluble sulfide precipitation pilot plant.

Throughout the testing period, feed to the pilot unit (a portion of effluent from the existing hydroxide treatment plant) approximated 45 gallons per minute. Ferrous sulfide reagent and polymer were continuously fed into the precipitator influent. As shown in Figure III, the flow path of the wastewater is downward, into the mixing and reactor zone of the precipitator. Near the bottom of the precipitator, a horizontal agitator pulls a certain amount of previously settled

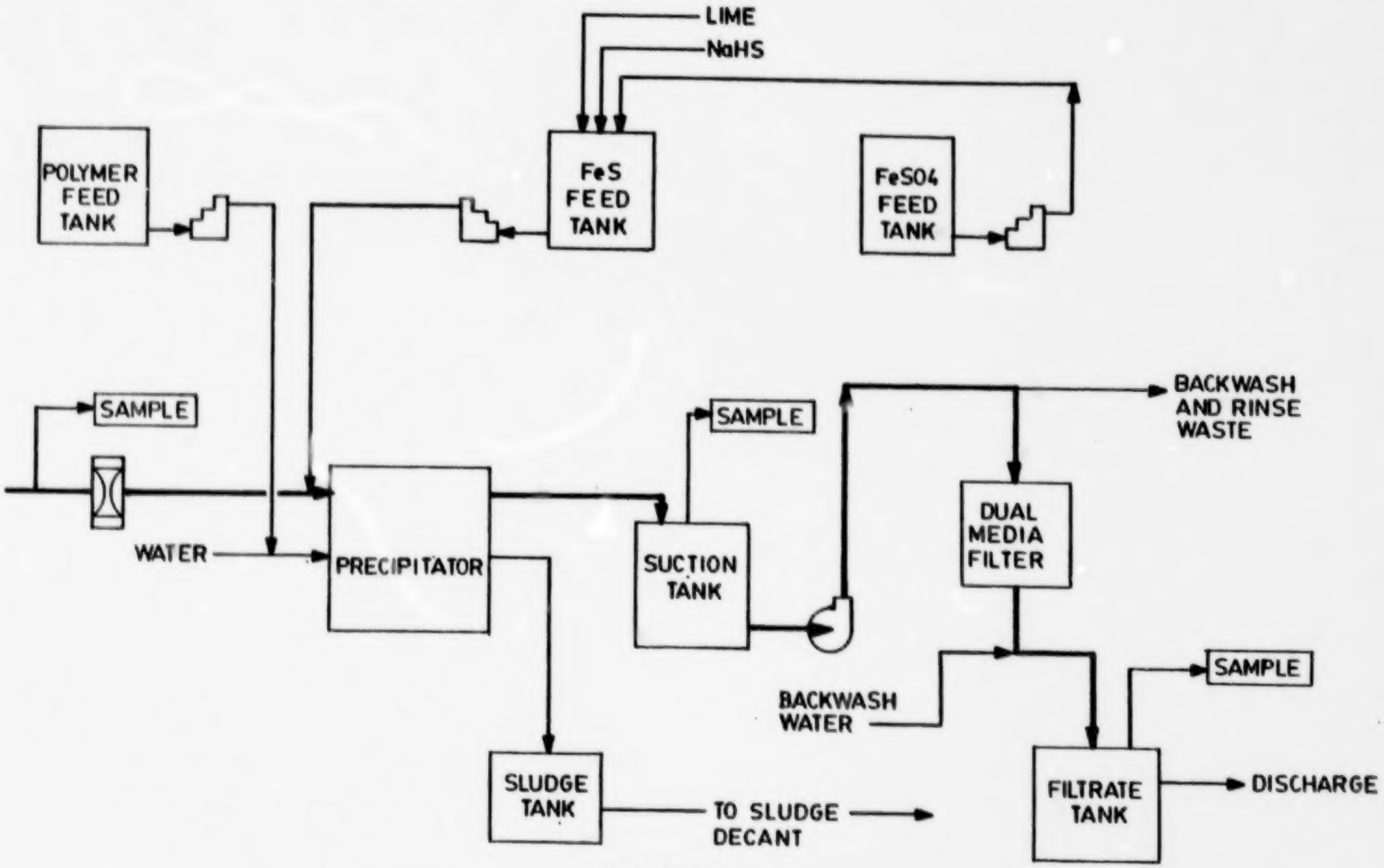
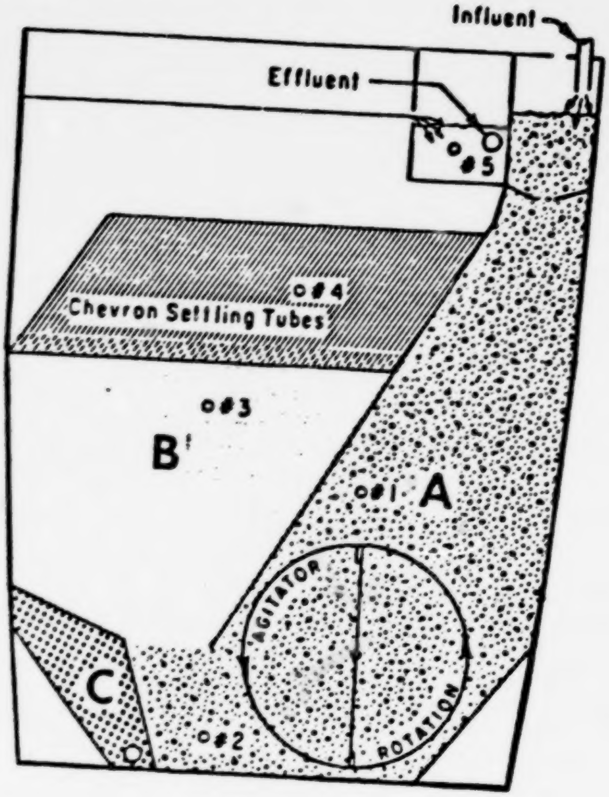

LIME
NaHS
POLYMER FEED TANK
FeS FEED TANK
FeS04 FEED TANK
SAMPLE
WATER
PRECIPITATOR
SAMPLE
SUCTION TANK
BACKWASH AND RINSE WASTE
DUAL MEDIA FILTER
BACKWASH WATER
SAMPLE
SLUDGE TANK
TO SLUDGE DECANT
FILTRATE TANK
DISCHARGE

FIGURE II
INSOLUBLE SULFIDE PRECIPITATION PROCESS
PILOT PLANT FLOW SCHEMATIC


Influent
Effluent
o #5
o #4
Chevron Settling Tubes
o #3
B
o #1
A
AGITATOR
ROTATION
C
o #2

CROSS SECTION OF PRECIPITATOR

A. Mixing and Reaction Zone.

B. Settling Zone.

C. Concentrator Zone.

FIGURE III

precipitate upward and back into the mixing and reaction zone to allow contact between old and newly precipitated materials. By varying the speed of the agitator, the concentration in the mixing and reaction zone can be varied from three to nine times that of the amount of material being newly precipitated. Further, the sludge blanket also provides additional contact with the precipitated material and at the same time, provides for upflow filtration of the liquid through the blanket. Heavier materials settle into the sludge concentrator zone prior to removal from the precipitator. To insure nearly complete utilization of the added chemical reagents, the sludge blowoff header requires flush back prior to sludge blowdown. This pushes precipitated material back up into the sludge blanket and ensures removal of only the heaviest materials. During pilot testing, this operation proved very effective.

The pilot plant set-up directed precipitator overflow to a pump suction tank from which the wastewater was pumped at 15 gallons per minute through the dual media filter. Filter effluent and excess flow to the suction tank was discharged to the Attleboro plant's outfall.

During the test period, fresh batches of ferrous sulfide and polymer solutions sufficient for 24 hours operation were prepared daily. The entire system was operated 24 hours per day for a total of 30 working days. The system was not run during weekends or designated plant shutdowns. Filter backwash was carried out once a day.

SAMPLING AND DATA COLLECTION

Throughout testing, eight hour composite samples were collected from the filtered effluent. Correspondingly, influent samples to the precipitator were also collected. All samples were analyzed in the laboratory for the metals limited by the discharge permit. In addition, four 24 hour composite samples were also collected, preserved and sent for independent analysis. Toxicity tests were also conducted on these 24 hour composite samples following EPA approved procedures.

Parameters which were also monitored included flow rate and pH of the influent and effluent samples for complete evaluation of the process. The ferrous sulfide feed was adjusted on the basis of total metal concentrations in the influent and, at times, were confirmed through jar tests.

ANALYTICAL PROCEDURES

Analyses of all collected samples were performed in TI's laboratory where inductively coupled plasma spectometry was primarily used. In addition, the 24 hour composite samples taken for toxicity testing were also analyzed using flame and graphite furnace atomic absorption spectrometry by Enviro-Systems Incorporated, TI's consultant for the toxicity testing program.

RESULTS AND CONCLUSIONS

PILOT TESTING PERFORMANCE

Influent Feed

The metal finishing process wastewaters at Texas Instruments were found to be highly variable in metal constituents during the course of the pilot testing program. Wide concentration variations were characteristic of samples collected from within the existing treatment system final clarifier and from the upstream final neutralization tank, both of which were a source of waste feed to the pilot unit during the different phases of testing. This variation in influent feed characteristics did not present a major problem to the insoluble sulfide precipitation process due primarily to the capabilities of the sludge blanket precipitator. Only slight adjustments in chemical feed rates were required based on periodic jar tests of the influent feed.

Metal Removal Efficiencies

Tables III and IV compare the quality of treated effluent, on the basis of an eight hour shift average, with respect to the draft and final U.S. EPA limits in the discharge permit. These results of the pilot testing program indicate that the insoluble sulfide precipitation process produces a quality effluent consistent in meeting the final EPA limits for zinc, cadmium, iron, copper, and chromium. Since the process also demonstrated relatively high removal efficiencies for boron, tin, silver, lead, nickel and aluminum, it is believed that full compliance with the discharge permit limits for these metals can be achieved by Texas Instruments through source reduction and in-plant controls in addition to advanced treatment by insoluble sulfide precipitation.

pH

The values of influent waste pH were consistently well adjusted within the optimum range of 8 to 9 pH units prior to the wastewater entering the pilot unit. The process chemistry within the precipitator reduced the effluent pH by at least 0.5 pH units. A further reduction of 0.2 pH units was realized in the filtered effluent. Overall, the precipitated and filtered effluent was maintained at a slightly alkaline pH (approximately 8.0 pH units).

Chemical Consumption

A comparison of actual ferrous sulfide feeds with theoretical demands indicated that the process pilot unit was constantly fed with a surplus of the ferrous sulfide slurry throughout the testing period. By analyzing the metal constituents and concentrations in the feed wastewater and calculating the stoichiometric requirements of these metals, the theoretical demand for ferrous sulfide could be

TABLE III

SUMMARY OF THE INSOLUBLE SULFIDE PILOT TEST PERFORMANCE
(SHIFT AVERAGE FOR THE PERIOD OF 6/7/85 TO 7/12/85)

	Zn	B	P	Cd	Fe	Sn	Ag	Cu	Pb	Ni	Al	Cr-T
Pilot Unit Feed	361	615	1,805	53	906	171	681	2,125	204	1,010	3,778	3,834
Precipitator Effluent	35	263	641	32	495	29	24	77	100	162	784	22
Final Filter Effluent	22	245	605	12	63	26	24	17	81	116	810	14
Draft EPA Limits	500	15	1,000	25	1,750	10	8	150	10	150	40	130
Final EPA Limits	400	2,000	1,000	25	1,750	20	7	150	31	170	1,000	190
Percent of Time Final Effluent Below EPA Draft Limits	100	0	90	100	100	50	(1)	100	50	75	0	100
Percent of Time Final Effluent Below EPA Final Limits	100	100	93	100	100	73	(1)	100	(1)	77	80	100
Average % Removal by Precipitator	90	57	64	40	45	83	96	96	51	84	79	99
Overall Process % Removal	94	60	66	77	93	85	97	99	60	89	79	99

NOTE:

(1) Denotes values which could not be assessed because analytical instrumentation detection limits exceeded the EPA limits.

(2) Metal ion concentrations are expressed in micrograms per liter.

TABLE IV

SUMMARY OF THE INSOLUBLE SULFIDE PILOT TEST PERFORMANCE
(SHIFT AVERAGE FOR THE PERIOD OF 8/26/85 TO 8/30/85)

	Zn	B	P	Cd	Fe	Sn	Ag	Pd	Cu	Pb	Ni	Al	Cr-T
Pilot Unit Feed	125	-	704	-	360	126	122	-	540	108	498	3,625	1,025
Precipitator Effluent	34	490	641	21	178	27	15	11	64	60	146	2,485	16
Final Filter Effluent	23	490	594	16	34	17	13	10	18	46	91	2,208	10
Draft EPA Limits	500	15	1,000	25	1,750	10	8	1,050	150	10	150	40	130
Final EPA Limits	400	2,000	1,000	25	1,750	20	7	1,050	150	31	170	1,000	190
Percent of Time Final Effluent Below Draft EPA Limits	100	0	100	90	100	55	(1)	100	100	(1)	90	0	100
Percent of Time Final Effluent Below Draft EPA Limits	100	100	100	90	100	73	(1)	100	100	(1)	90	18	100
Average % Removal by Precipitator	73	-	10	-	50	79	88	-	88	44	71	31	98
Overall Process % Removal	82	-	15	-	90	87	89	-	97	57	82	39	99

NOTE:

(1) Denotes values which could not be assessed because analytical instrumentation detection limits exceeded the EPA limits.

(2) Metal ion concentrations are expressed in micrograms per liter.

estimated. These calculated demands did not include the requirements for non-metallic species such as phosphorus and boron since their stoichiometric requirements are not clearly understood. However, based on these estimates, it was determined that an average of 3 to 5 times the theoretical ferrous sulfide requirement was supplied during the demonstration test runs.

The polyelectrolyte consumption also fluctuated. In some cases where high concentrations of suspended solids were present in the influent wastewater, increased polyelectrolyte usage was required. Results of this study indicated that approximately 0.5 to 1 mg/l of polyelectrolyte would be adequate for treatment of the existing treatment system effluent.

TOXICITY TESTING RESULTS

One of the principal objectives of the pilot test program was to determine if TI's wastewater effluent, by undergoing advanced treatment, could be rendered non-toxic for discharge to the surface water outfall, Coopers Pond. As previously described, performance of the insoluble sulfide process was monitored for biological toxicity by scheduled sampling of the treated, filtered effluent. The results of toxicity testing of 24 hour composite samples are shown in Table V which also presents the concentrations of wastewater constituents.

Results of the acute bioassays clearly indicate that the insoluble sulfide precipitation process should produce an effluent which will consistently pass the toxicity tests required by the NPDES permit. Two of the acceptable chronic test results were encouraging because both samples were obtained during periods when the pilot unit was processing a relatively contaminated waste stream resulting from process bath dumps.

Recognizing that the toxicity tests (utilizing the daphnid, Daphnia pulex, as the acute test organism) are subjective, it is difficult to establish reasons based on reduction of metal concentrations alone for a specific survival rate. However, the following explanations are offered as most probable:

- With the insoluble sulfide precipitation process, only the heavy metals are removed by precipitation without any other significant change in the pH or in the chemical composition of the treated wastewater.
- The process does not add any detrimental compounds to the wastewater while removing metals.

OPERATING COSTS

Operating costs for a 600 gallon per minute insoluble sulfide precipitation system as an advanced polishing treatment process at TI have been estimated to be \$0.70 per 1,000 gallons of wastewater treated. Based upon data collected during pilot testing, this figure includes \$0.15/1,000 gallons for chemical costs. TI's estimated costs for power (\$0.10/1,000 gallons), sludge disposal (\$0.25/1,000 gallons) and operating personnel (\$0.20/1,000 gallons) were added to the chemical costs to derive the overall operating costs of the process.

TABLE V

SUMMARY OF RESULTS FROM REPRESENTATIVE ACUTE AND CHRONIC EFFLUENT BIOASSAYS: INSOLUBLE SULFIDE PRECIPITATION PROCESS

	TEST SERIES			
PARAMETER	6/20/85	6/26/85	7/3/85	7/12/85
Acute LC-50 (1)	100%	100%	100%	100%
Acute NOAEL (2)	100%	50%	100%	100%
Chronic NOAEL (3)	12.5%	20%	60%	80%
Hardness (mg/l)	76	48	51	66
Alkalinity (mg/l)	81	56	71	74
Ammonia (mg/l)	0.01	0.01	0.7	0.9
Residual Cl (mg/l)	0	0	0	0
pH (units)	7.66	7.80	7.94	7.70
Ag (mg/l)	0.005	0.025	0.0008	0.0005
Al (mg/l)	0.52	0.52	0.71	0.32
Cd (mg/l)	0.004	0.006	0.002	0.008
Cr (total) (mg/l)	0.0005	0.035	0.0005	0.0005
Cu (mg/l)	0.009	0.041	0.014	0.005
Fe (mg/l)	0.064	0.23	0.29	0.055
Ni (mg/l)	0.12	0.20	0.12	0.09
Pb (mg/l)	0.001	0.043	0.002	0.023
Se (mg/l)	0.01	0.01	0.01	0.01
Sn (mg/l)	0.01	0.045	0.01	0.01
Zn (mg/l)	0.008	0.028	0.004	0.005
Cr $(^{+6})$ (mg/l)	0.0005	0.035	0.0005	0.0005
CN (mg/l)	0.06	0.21	0.09	0.06
F (mg/l)	4.7	1.8	1.1	1.1
P (mg/l)	0.69	1.8	1.1	0.48
Pd (mg/l)	0.005	0.005	0.005	0.005
B (mg/l)	0.6	0.5	0.5	0.27

(1) LC-50 is the strength of the treated wastewater sample in which 50 percent of the test organisms survive 48 hours.

(2) NOAEL (Non-Observable Acute Effect Level) specifies the strength of the treated wastewater sample in which a major population of the test organism survives 48 hours.

(3) Chronic No Effect Level is the strength of the treated wastewater sample in which the normal life production cycle of juveniles of the major population of the test organism is unaffected through 7 days of the bioassay testing.

CONCLUSIONS

The pilot testing, toxicity testing and operating cost evaluations convinced Texas Instruments that an upgrade of their existing wastewater treatment system should include insoluble sulfide precipitation as an advanced treatment process in order to meet the new NPDES Permit requirements. Final design of the wastewater treatment upgrade has been completed. The design has taken into account licensing considerations, system maintainability and reliability, and TI's commitment to total compliance with all local, state and federal environmental codes.

The advanced treatment plant will include a new 10,000 ft^2 building addition which will house two 300 gallon per minute equipment trains consisting of inclined plate clarifier/thickeners, sludge blanket precipitators, dual media filters and chemical feed systems. The treatment system will also include two new 250,000 gallon holding/equalization tanks to receive flow from the existing treatment plant before the wastewater is directed to the new advanced treatment system.

The new treatment plant is currently under construction. Startup is expected in mid-1987.

NOTES

1. SULFEX^{TN} is a patented process of the Permutit Company.

2. The term "Precipitator" used throughout this report refers to a proprietary upflow, solids contact reactor-settles unit manufactured by the Permutit Company.

ACKNOWLEDGEMENTS

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THE PERFORMANCE OF ANALYTICAL TEST KITS ON METAL FINISHING WASTEWATER SAMPLES

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ABSTRACT:

Stringent Federal Pretreatment Regulations and NPDES Permit Requirements have created a need for close, constant monitoring of the pollutant concentrations of metal finisher's effluents. Large captive and a few job shops have invested the large sums of money required to construct analytical laboratories sophisticated enough to perform analytical monitoring using EPA approved procedures. Other, less endowed, and less sophisticated metal finishers have resorted to the use of inexpensive test kits for monitoring their discharge. There are numerous suppliers of these kits and their number is expanding with this surge in demand. The purpose of this investigation was to perform a study of the capabilities and ease of use of the most widely publicized kits and to compare them with the EPA approved methods of analysis.

This study was funded by the National Association of Metal Finishers (NAMF) in the interest of assisting their members in better monitoring the performance of their waste treatment systems.

For each analytical procedure, an attempt was made to include a variety of metal finishing sources that would have an effluent containing the parameter under consideration in concentrations below or near the Federal Pretreatment Guidelines.

Brand new test kits and supplies were purchased from their manufacturers for this study. Since the final report on this study is currently under review by NAMF and in the interest of maintaining AESF policy on commercialism, the names of the kit manufacturers are not disclosed in this report. This information will be available from NAMF when the final report is approved.

The manufacturers of the test kits were not aware of this study, although some may have obtained notices through membership in NAMF.

The study concentrated on test kits often used in compliance monitoring by metal finishers. The test kits evaluated were for the determination of heavy metals (copper, zinc, cadmium, lead, nickel, total and hexavalent chromium), cyanide, fluoride, pH, and total phosphorous.

The study was performed under the supervision of the author utilizing the resources of the author's analytical laboratory which is certified by the Illinois Environmental Protection Agency.

ANALYSIS OF HEAVY METALS:

For the analysis of heavy metals, we chose 15 separate metal finishing sources in the Chicago area. Metal finishing sources included job, captive plating shops, and circuit board manufacturers. For analysis of other parameters, we sometimes were limited to fewer sampling sources due to their scarcity in our area.

Each sample was prepared and analyzed in accordance with the instructions provided with the test kit. Each sample was also analyzed using the EPA approved method of sample preparation and analysis.

Also analyzed were "standard" wastewater samples prepared by diluting known concentrations of heavy metals purchased from a reputable supplier. These simple standards were used to determine if the kits performed better in the absence of the morass of interferences normally encountered in metal finishing waste streams and to determine the repeatability of the test kit.

Kits were compared to EPA approved analytical procedures for accuracy, repeatability and ease of use using the following procedures:

ACCURACY

Kits were evaluated for accuracy using the following technique:

1. The absolute difference between the EPA procedure analytical value and that obtained with the kit on real samples was calculated (example: Copper Analysis, Sample 13/Kit 1 absolute difference is 0.6-.75 = -.15 = .15, absolute means that a negative number is counted as positive).
2. The differences on all 15 samples were added together.
3. The total from step 2 was divided by the total number of samples analyzed to obtain an average difference.
4. The kit with the lowest average difference was rated highest. A formula for calculating this rating is:

$$\text{RATING} = \left[\frac{A - B}{A} \times 10 \right] + 1$$

A = Average difference of all kits.
B = Average difference of given kit.

REPEATABILITY

Kits were rated for repeatability using the following technique:

1. A simple standard near the regulated concentration was analyzed six times.

2. The differences between sequential analytical results on these repetitions were added up (example 3.1, 3.1, 3.0, 3.2, 3.2, 3.5 yields a sum of .6).

3. The total obtained in step 2 was subtracted from an arbitrary value of 10. Perfect repeatability (a zero in step 2) would then yield a perfect 10 rating.

EASE OF USE

Each kit was arbitrarily rated for ease of use based on the number of analytical steps that needed to be taken to perform the analysis and the difficulty of each step. Not included in this rating was the undesirable use of dangerous chemicals with some kits. The effect of the use of dangerous chemicals upon the usability of the kit should be evaluated by the user. The kit that used the fewest number of analytical steps and that avoided procedures such as weighing on an analytical balance and volumetric dilutions was rated at 10 (very easy to use). Kits that had more steps and complications had points subtracted from 10.

COPPER: (see Tables A & a)

Of seven kits evaluated, only one provided sufficient accuracy to warrant consideration for direct use as a monitoring tool on metal finishing wastewater. A general lack of accuracy was attributed to the presence of solids in the samples that were not solubilized by the acid digestion procedure provided by the kits. Several kits provided no instructions for sample preparation prior to analysis and these kits were typically the lowest in accuracy.

The EPA approved sample preparation procedure for analysis of heavy metals involves transferring a 100 mL sample from a well shaken bottle into a 250 mL beaker. 5 mL of 1:1 reagent grade hydrochloric acid is added and the sample is mixed, then heated on a hot plate to a volume of 15-20 mL (without boiling). The sample is then diluted back to 100 mL in a volumetric flask prior to analysis.

None of the kits provided instructions for an acid digestion as rigorous as the EPA approved method. This is understandable since the EPA digestion typically takes between 2-3 hours to complete while the kits are meant to provide fast answers. Accuracy is thereby sacrificed for speed.

All seven kits had good repeatability and were easy to use. The easiest to use kits (#3 & #4) had all reagents inside an evacuated glass vial with a thin glass tip. When the tip was broken by immersion in the test sample, a precise amount of sample was "automatically" drawn inside the vial. The vial was then rotated by hand to mix the sample and chemicals for color development. The intensity of the developed color was then measured either visually or in a colorimeter.

ZINC: (see Tables B & b)

Two of five kits evaluated provided accuracy that was sufficient for consideration as monitoring techniques on metal finishing wastewater samples.

Insufficient accuracy was again a result of incomplete digestion of undissolved solids by sample preparation instructions or the total absence of instructions for sample preparation.

All five kits rated high on repeatability. This would indicate that the kits could be used for routine monitoring if a correction factor could be established by comparison with the EPA procedure. Two of the kits rated low on ease of use due to the need for shaking for 15 seconds exactly (a difficult task) (kit 5) and for the inconvenient handling of dangerous reagents such as cyanide and formaldehyde (kit 6).

TABLE A

COMPARISON OF WASTEWATER ANALYSIS FOR COPPER USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	USEPA Approved Procedure	Kit 1	Kit 2	Kit 3	Kit 4	Kit 5	Kit 6	Kit 7
1	5.3	2.7	4.6	3.5	2.71	4.0	3.6	3.5
2	0.8	0.5	0.64	0.4	0.13	0.2	0.35	0.5
3	3.2	1.9	0.83	3.0	2.41	2.0	2.4	2.0
4	1.6	1.2	1.25	1.0	0.89	0.8	0.4	0.5
5	0.9	0.8	0.68	1.0	0.40	0.3	0.8	0.8
6	0.5	0.0	0.56	0.4	3.78	0.1	0.28	0.5
7	0.6	0.5	0.40	0.4	0.76	0.3	0.45	0.5
8	3.3	1.25	2.8	1.0	0.95	0.3	0.56	0.5
9	2.4	0.9	2.0	2.6	1.86	0.8	1.22	0.5
10	4.3	2.3	3.4	5.0	3.04	3.0	2.7	4.0
11	8.3	0.70	6.4	1.0	0.0	1.0	6.4	3.0
12	1.6	1.4	1.6	1.0	0.76	2.0	0.5	2.0
13	0.6	0.75	1.4	1.0	0.70	0.5	0.8	1.0
14	0.6	0.30	0.6	0.1	0.0	0.1	0.2	0.0
15	1.9	1.2	1.5	1.0	1.23	0.3	0.8	0.5
STD 1.0	1.0	1.2	1.1	1.0	0.95	0.75	1.1	1.5
STD 3.0	3.1	2.9	2.9	3.0	3.0	3.0	1.7	3.0
STD 5.0	5.1	4.5	4.0	5.0	5.3	5.0	3.2	5.0
STD 3.0	3.1	2.7	3.0	3.0	2.95	3.0	1.7	3.5
STD 3.0	3.1	2.5	3.0	3.0	2.93	3.0	1.9	3.5
STD 3.0	3.1	2.7	3.0	3.0	3.04	3.0	1.9	3.5
STD 3.0	3.0	2.6	2.9	3.0	2.93	3.0	1.9	3.0
STD 3.0	3.2	2.7	3.0	3.0	3.04	3.0	1.9	3.5
STD 3.0	3.1	2.7	2.9	3.0	2.93	3.0	1.7	3.5

TABLE 8

KIT RATINGS - COPPER IN METAL FINISHING WASTEWATER

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
1	2.2	9.4	9.5
2	6.9	9.8	9.0
3	3.0	10	10
4	1.0	9.6	9.8
5	2.7	10	8.0
6	4.4	9.6	7.5
7	4.2	8.0	9.5

*EPA approved procedure rated at 9.6 for repeatability on the same samples.

TABLE B

COMPARISON OF WASTEWATER ANALYSIS FOR ZINC USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	A.A.	Kit 2	Kit 4	Kit 5	Kit 6	Kit 7
1	1.4	0.14	0.14	0.4	0.41	0.
2	0.7	0.08	0.34	0.4	0.41	0.
3	18.0	9.7	9.7	0.	2.0	14.5
4	0.4	0.24	0.56	0.8	0.27	0.
5	0.2	0.07	0.43	0.4	0.18	0.
6	21.7	19.5	25.6	4.	0.69	4.5
7	0.3	0.95	0.31	0.	0.75	0.
8	1.1	0.17	0.46	0.	1.07	0.
9	0.4	0.33	0.84	0.	1.16	0.
10	0.8	0.33	0.31	0.4	0.3	0.
11	22.5	17.8	9.7	2.0	1.0	14.0
12	0.9	0.47	0.02	0.	0.32	0.*
13	0.9	0.63	0.97	0.4	1.16	0.5
14	0.1	0.8	0.25	0.4	0.06	0.
15	0.8	0.38	0.48	0.4	0.84	0.
STD 1.0	1.0	0.68	1.03	0.8	0.56	1.0
STD 3.0	3.0	2.9	2.64	1.6	1.6	3.5
STD 5.0	4.9	5.1	3.46	2.4	2.2	6.0
STD 3.0	3.0	2.87	2.73	1.6	1.6	3.5
STD 3.0	3.0	2.93	2.73	1.6	1.6	3.5
STD 3.0	2.7	2.7	2.64	1.6	1.6	3.0
STD 3.0	3.0	2.9	2.64	1.6	1.8	3.0
STD 3.0	3.0	2.83	2.56	1.6	2.0	3.5
STD 3.0	2.7	2.83	2.48	1.6	1.8	3.5

*Kit 7 on Sample #12 gave inconclusive results. A definite color change occurred. However, the color in no way matched the color standards. Take as 0 ppm.

TABLE b

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
2	7.6	9.4	8.0
4	6.2	9.7	9.0
5	3.6	10	6.0
6	1.0	9.4	6.5
7	2.5	9.0	9.0

*The EPA approved procedure rated at 9.1

CADMIUM: (see Tables C & c)

Only one of three kits provided accuracy sufficient for monitoring use on metal finishing wastewaters. Poor accuracy on the other two kits was attributed to poor sample preparation techniques and an apparent inability of the extraction reagents to fully extract cadmium from the sample.

All three analytical procedures utilized extractions in seperatory funnels with chemicals that can be quite hazardous to use (cyanide, chloroform). Often, emulsions were formed that made delineation between aqueous and chloroform layers very difficult.

LEAD: (see Tables D & d)

Two of three kits tested (#2 and #7) had a high degree of accuracy and repeatability. All three kits utilized dithizone as the color developing reagent. The kits exhibiting the greater accuracy employed cyanide and chloroform in the analytical procedure. Kit #7 required a slight procedural modification before satisfactory results were obtained. The modification involved the addition of excess ammonium hydroxide to the extraction funnel. While Kit #2 provided all necessary reagents, Kit #7 required that reagents be made up and not all reagents were supplied with the kit. The user would need to have an analytical balance to prepare some of these.

Kit #5 did not utilize cyanide as a reagent and the extraction solvent was carbon tetrachloride resulting in a somewhat "safer" analytical kit. Kit #5 was the easiest to use kit and did not involve the use of a separatory funnel. An analysis using Kit #5 involved five short steps consuming about four minutes. This would be an ideal kit to use if correlation with EPA approved procedures could be shown. Kits #2 and #7 required 7 and 11 analytical steps and consumed 30 and 10 minutes respectively.

NICKEL: (see Tables E & e)

Five analytical kits were evaluated for use as nickel concentration monitoring devices. Only one kit (#5) rated high on accuracy, repeatability and ease of use.

Kit #5 did not involve the use of an extraction procedure and utilized dimethylglyoxine as the color developing reagent. This Kit involved nine analytical steps and required about 22 minutes per determination. The other kits ranged from 5 to 12 analytical steps and 20 to 40 minutes.

Kit #2 utilized a chloroform extraction of a developed color using a separatory funnel.

Kit #6 was similar to Kit #5, but utilized a colorimeter to measure color intensity.

Kit #7 also used dimethylglyoxine for color development.

Kit #8 used dimethylglyoxine to precipitate the nickel. The volume of the precipitate produced was used to measure the concentration of nickel.

TABLE C

COMPARISON OF WASTEWATER ANALYSIS FOR CADMIUM USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	A.A.	Kit 2	Kit 5	Kit 7
1	0.1	0.1	*0.1	0.1
2	*0.1	0.03	*0.1	0.1
3	*0.1	0.02	1.	0
4	0.7	0.60	0.4	0.1
5	*0.1	0.01	*0.1	0.1
6	0.6	0.36	0.4	0.3
7	*0.1	0.01	0	0
8	2.5	2.4	0	0.6
9	*0.1	0.05	0.2	0
10	*0.1	0.01	0.1	0
11	4.0	2.7	0	0.5
12	*0.1	0.02	0	0
13	3.8	3.8	3.0	1.0
14	*0.1	0.02	0	0
15	0.1	0.05	0	0
STD 1	1.0	0.98	0.5	0.3
STD 2	2.0	2.1	1.8	0.6
STD 5	5.0	5.2	5.0	2.0
STD 2	2.0	2.1	2.0	1.0
STD 2	2.0	2.0	2.0	0.6
STD 2	2.0	2.2	2.0	0.8
STD 2	2.0	2.1	1.8	0.6
STD 2	2.0	2.1	1.8	0.6
STD 2	2.0	2.4	2.0	0.8
STD 2	2.0	2.2	1.8	0.7

*Denotes "less than" (below detectable limit of procedure used).

TABLE c

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
2	8.5	9.1	7.5
5	1.6	9.4	8.0
7	1.0	8.9	6.0

*The EPA approved procedure rated at 10.

TABLE D

COMPARISON OF WASTEWATER ANALYSIS FOR LEAD USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	A.A.	Kit 2	Kit 5	Kit 7**
1	0.3	0.11	0	0.3
2	0.2	0.22	0	0.2
3	*0.1	0.05	0	0
4	*0.1	0.10	0.6	0
5	0.1	0.18	0	0
6	*0.1	0.05	3.0	0
7	*0.1	0.09	0	0
8	*0.1	0.05	0	0
9	*0.1	0.05	0	0
10	0.5	0.62	0	0.6
11	0.7	0.63	0.1	0.6
12	0.4	0.46	0.4	0.5
13	*0.1	0.06	0.1	0
14	*0.1	0.13	0	0
15	1.5	1.6	1.5	1.4
STD 0.5	0.50	0.53	0.5	0.5
STD 0.5	0.50	0.55	0.5	0.5
STD 1.0	1.0	1.1	0.9	1.0
STD 1.0	1.0	1.1	0.9	1.0
STD 0.5	0.5	0.57	0.5	0.6
STD 0.5	0.5	0.55	0.4	0.6
STD 0.5	0.5	0.60	0.4	0.6
STD 0.5	0.5	0.50	0.4	0.6
STD 0.5	0.5	0.56	0.4	0.6
STD 0.5	0.5	0.52	0.4	0.6

*Denotes "less than" (below detectable limit of procedure used).
**Modified Procedure

TABLE 6

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
2	9.6	9.7	7.5
5	6.6	9.9	9.0
7	9.7	10.0	8.5

*The EPA approved procedure rated at 10.

TABLE E

COMPARISON OF WASTEWATER ANALYSIS FOR NICKEL USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	A.A.	Kit 2	Kit 5	Kit 6	Kit 7	Kit 8
1	*0.1	0.05	0.	1.0	1.	0.
2	*0.1	0.17	0.	0.2	1.	0.
3	3.6	0.6	1.0	1.0	1.	0.
4	*0.1	0.07	0.	0.2	1.	0.
5	0.4	0.02	0.5	0.7	1.	1.
6	*0.1	0.18	0.	1.0	1.	0.
7	5.6	2.7	6.0	8.0	4.	2.
8	5.0	3.5	5.0	7.6	1.	3.
9	1.4	1.74	1.0	2.2	1.	2.
10	0.1	0.03	0.	0.2	1.	3.
11	1.9	6.0	3.0	4.3	1.	0.
12	*0.1	0.28	0.	0.4	1.	0.
13	*0.1	0.25	0.	0.2	1.	0.
14	2.6	4.0	3.0	5.0	1.	2.
15	3.8	4.0	4.0	6.0	1.	2.
STD 0.5	0.5	0.4	0.5	0.6	1.	**
STD 1.0	1.0	0.8	1.0	1.1	1.	1.0
STD 3.0	3.0	2.6	3.0	4.5	3.	2.5
STD 5.0	5.0	4.8	4.0	7.5	1.	4.7
STD 3.0	3.0	2.8	3.0	5.0	2.	2.5
STD 3.0	3.1	2.6	4.0	5.0	2.	2.5
STD 3.0	3.0	2.9	3.0	5.0	1.	2.5
STD 3.0	3.0	2.7	3.0	4.0	2.	2.5
STD 3.0	3.0	2.8	3.0	5.0	1.	2.5

*Denotes "LESS THAN" (Below detectable limit of procedure used).
**Kit cannot analyze below 1.0 mg/L.

TABLE e

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
2	6.8	9.2	4
5	9.3	8.0	9
6	5.7	9.0	8
7	1.0	7.0	6
8	5.7	10	9.5

*EPA procedure rated at 9.8

TOTAL AND HEXAVALENT CHROMIUM: (see Tables F, f, FF, & ff)

Of four kits evaluated, only two (Kits #1 & #2) had a reasonable measure of accuracy, repeatability, and ease of use.

Kits #1 & #2 were made by the same manufacturer, the only difference being the use of a colorimeter instead of a visual comparator for Kit #2. Kits #1 & #2 involved a total of 11 analytical steps and an elapsed analytical time of about 40 minutes. Kits #1 & #2 also were the best performing kits for hexavalent chromium analysis, utilizing similar analytical procedures.

TOTAL CYANIDE: (see Tables G & g)

The very properties that make cyanide such a useful chemical also make it difficult to destroy and analyze for. Cyanide forms varying complexes with most all regulated metals. Some of these complexes are so stable that even boiling in dilute acid does not completely destroy them.

Since most analytical procedures measure the presence of cyanide in one and only one form of that chemical, one cannot expect a test kit to detect total cyanide concentration, and it is total cyanide that is regulated.

The chief anticipated use of a test kit for cyanide is therefore as a method of monitoring the effluent from a waste treatment system once a correlation between total cyanide and the kit analysis is established. Therefore, the major expectation from a test kit should be good reproducibility which will allow the development of correction factors.

Based on this study, three analytical test kits warrant consideration for use as monitoring tools on metal finishing wastewaters but only if an acid distillation* is employed prior to analysis to break up complexed cyanide. Without this acid distillation no reasonable amount of accuracy was obtained.

Kit #2 involved seven analytical steps and an elapsed time of about 30 minutes. An acid distillation would add about 2 hours to the elapsed time.

Kit #5 involved ten analytical steps and an elapsed time of about 10 minutes without the distillation.

Kit #9 involved seven analytical steps and only 5 minutes of elapsed time. Kit #9 utilized test strips similar to pH papers while the other kits attempted to develop colored solutions for intensity measurement or a colorimeter.

We had difficulty obtaining any suitable color development with Kit #7 and after several attempts at corrections including discussions with the manufacturer, we gave up.

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*See "Standard Methods for the Examination of Water and Wastewater", 16th Edition Method 412B.

TABLE F

COMPARISON OF WASTEWATER ANALYSIS FOR TOTAL CHROMIUM USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	A.A.	Kit 1	Kit 2	Kit 5
1	9.2	9.2	7.5	2.7
2	4.5	3.8	2.0	0.6
3	1.0	0.5	0.1	0.3
4	*0.1	0	0.04	0
5	*0.1	0	0.02	0
6	3.5	1.5	1.2	0.5
7	4.5	1.5	1.7	0.6
8	*0.1	0	0	0
9	0.3	0.6	0.3	0.1
10	1.5	1.5	1.2	0.6
11	5.5	4.6	3.6	1.6
12	0.7	0.6	0.12	0
13	*0.1	0	0	0
14	2.9	3.9	2.5	0.4
15	*0.1	0	0	0
STD 1	1.0	1.1	1.0	0.1
STD 5	5.0	5.0	4.8	2.1
STD 10	10.5	11.6	8.8	5.7
STD 5	5.0	4.6	4.8	2.8
STD 5	5.1	5.0	5.2	2.8
STD 5	5.2	4.2	5.5	2.1
STD 5	4.9	3.8	5.5	2.1
STD 5	5.0	5.8	5.6	2.8
STD 5	5.1	5.8	4.5	2.7
STD 5	5.0	4.6	4.8	2.1

*Denotes "LESS THAN" (Below detectable limit of procedure used).
NOTE: No readable results obtained with Kit 7.

TABLE f

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
1	7.8	5.6	10
2	5.9	7.8	8.5
5	1	7.9	7.0
7	0	0	7.0

*The EPA Approved Procedure rated at 9.2.

TABLE FF

COMPARISON OF WASTEWATER ANALYSIS FOR HEXAVALENT CHROMIUM USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	EPA Approved Procedure	Kit 1	Kit 2	Kit 5	Kit 6
1	9.0	9.2	6.3	0.2	4.3
2	5.0	5.0	4.0	0.4	4.6
3	1.0	0.33	0.31	0	0.1
4	*0.1	0	0.04	0	0.1
5	*0.1	0	0.02	0	0
6	2.3	2.0	1.4	0.3	0.7
7	4.0	3.4	3.0	0.9	3.9
8	*0.1	0	0	0	0.1
9	*0.1	0.40	0.4	0.3	0.5
10	1.1	1.0	0.95	0.3	1.1
11	5.3	1.8	1.8	0	0.8
12	0.7	0.6	0.49	0.2	0
13	*0.1	0	0.01	0	0
14	1.9	1.9	1.8	0.6	0.9
15	*0.1	0	0	0	0

*Denotes "LESS THAN" (Below detectable limit of procedure used).

TABLE ff

KIT	ACCURACY	EASE OF USE
1	8.9	10
2	7.2	8.5
5	1.0	7.0
6	5.6	7.0

TABLE G

COMPARISON OF WASTEWATER ANALYSIS FOR CYANIDE USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	EPA Approved Procedure	Kit 1	Kit 2	Kit 5	** Kit 7	Kit 9
1	30.5	0.22	15.	0.15	—	3
2	10.0	0.08	3.5	0	—	1
3	0.90	0.	1.6	0.25	---	0
4	1.25	0.03	1.7	0.	---	0
5	8.25	0.06	2.1	1.5	---	1
6	7.00	0.06	2.4	0.35	---	1
7	0.25	0.0	0.09	0.	---	0
8	0.35	0.03	0.13	0.	—	0
9	2.05	0.0	0.01	0.05	—	0
10	*0.05	0.0	0.005	0.	—	0
11	0.25	0.05	0.028	0.	—	0
12	*0.05	0.03	0.01	0.2	---	0
13	*0.05	0.0	0.007	0.	—	0
14	*0.05	0.0	0.009	0.	—	-
15	*0.05	0.03	0.013	0.	—	0
STD 0.1	0.09	0.095	0.05	0.	—	0
STD 0.5	0.40	0.40	0.24	0.65	—	0
STD 1.0	0.9	0.8	0.5	1.0	—	1
STD 5.0	5.0	2.0	2.6	5.5	---	3
STD 1	1.0	0.9	0.57	1.0	---	1
STD 1	1.0	0.7	0.60	1.1	---	1
STD 1	1.0	0.7	0.55	1.2	---	1
STD 1	1.0	0.7	0.55	1.0	---	1
STD 1	0.9	0.9	0.60	1.0	---	1
STD 1	0.9	0.8	0.55	1.0	---	1

*Denotes "LESS THAN" (Below detectable limit of procedure used)

TABLE 9

KIT	ACCURACY		REPEATABILITY*	EASE OF USE
	No distillation	With distillation		
1	1.0	1.0	9.5	9.0
2	4.9	8.9	9.8	8.5
5	1.3	7.9	9.6	7.0
7	0	---	0	5.0
9	1.9	8.3	10	10.0

*The EPA procedure rated at 9.9

TOTAL PHOSPHORUS: (see Tables H & h)

Three of seven kits rated high in accuracy, repeatability and ease of use.

Kit #2 required 5 analytical steps and only about 8 minutes of analytical time. Even without the persulfate digestion which is required by the EPA approved analytical procedure, this kit analyzed five of seven samples with reasonable accuracy. With the persulfate digestion no further performance improvement was obtained.

Kit #5 consisted of four analytical steps and used a visual comparator (as opposed to the colorimeter used by Kit #2). This made Kit #5 readily portable for measurement at remote sites. The time required for an analysis using Kit #5 was only about 5 minutes.

Kit #7 was also a "visual" analytical method requiring six analytical steps and about 5 minutes of elapsed time.

Both Kits 5 and 7 obtained reasonably accurate results on two of seven samples. Persulfate digestion did not further improve the accuracy obtained with these kits.

FLUORIDE: (see Tables I, IA, & i)

No test kit (out of four evaluated) rated high in accuracy even after a preliminary distillation* was performed on the wastewater samples analyzed. The preliminary distillation is tedious, requires expensive and delicate glassware, and is dangerous due to hot sulfuric acid which is employed.

pH ANALYSIS: (see Tables J & j)

Five kits sold for the purpose of pH analysis were evaluated. None of these performed adequately for close monitoring purposes over a broad range. We recommend consideration of the use of small hand held pH meters which are available at very low prices ($40) and perform extremely well.

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*"Standard Methods for the Examination of Water and Wastewater", 16th Edition Method 413.

TABLE H

COMPARISON OF WASTEWATER ANALYSIS FOR PHOSPHORUS USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	EPA Approved Procedure	Kit 1	Kit 2	Kit 3	Kit 4	Kit 5	Kit 6	Kit 7
1	585	2500	600	700	344	1000	2400	100
2	25.8	290	31.6	10	3.1	10.0	38	0.8
3	6.8	4.5	3.3	2.0	3.0	6.0	18	1.0
4	42.5	270	46.6	60	134	100	200	100
5	7.8	200	3.3	8	21.8	0	0	20
6	1600	4500	900	6000	4100	3000	4000	1700
7	85.0	240	60	8	195	200	100	1000
STD 0.5	0.6	2.0	1.6	1.0	1.4	2.0	*	0.8
STD 1	1.1	4.3	3.0	3.0	2.5	3.0	*	1.7
STD 5	5.0	26	16	5.0	6.0	10.0	22.0	6.0
STD 10	9.4	35	30	8.0	11.8	30	380	2.0
STD 1	1.2	4.0	3.0	2.0	2.7	3.0	22.0	1.8
STD 1	1.1	4.2	3.0	3.0	2.5	3.2	20.0	2.0
STD 1	1.0	4.1	3.0	3.0	2.8	3.0	22.0	2.0
STD 1	1.1	4.3	3.0	3.0	2.5	3.1	20.0	1.7
STD 1	1.0	4.2	3.0	2.0	2.5	3.0	20.0	2.0
STD 1	1.1	4.2	3.0	3.0	2.5	3.0	22.0	1.8

*Out of range - lower than detectable limit.

TABLE h

KIT	ACCURACY RATING	REPEATABILITY RATING*	EASE OF USE
1	1.0	9.4	8.0
2	9.6	10	7.5
3	2.8	7.0	9.8
4	5.7	9.2	9.5
5	7.4	9.4	7.5
6	3.2	2.0	6.0
7	8.2	9.0	4.0

*The EPA Approved Procedure rated at 9.5.

TABLE I

COMPARISON OF WASTEWATER ANALYSIS FOR FLUORIDE USING TEST KITS AND EPA APPROVED PROCEDURE

(NO DISTILLATION PRIOR TO KIT TEST)

Sample	EPA Approved Procedure	Kit 2	Kit 5	Kit 6	Kit 7
1	1.34	90	100	1.05	0
2	405	600	2.8	1.05	0.2
3	1.57	1.05	0.2	0.95	0
4	0.68	60	0	1.0	0
5	36.4	1.2	0.2	0.5	0.1
6	20.4	75	0	0.7	0
7	15.3	15	0	0.9	0.1
STD 0.5	0.52	0.4	0.3	0.5	0.2
STD 1.0	0.95	0.85	1.0	0.6	1.1
STD 2.0	2.3	1.6	2.2	1.8	2.2
STD 1	0.95	0.90	1	0.6	1.0
STD 1	0.90	0.90	1	0.65	1.0
STD 1	0.95	0.85	1	0.60	1.2
STD 1	0.95	0.90	1	0.60	1.1
STD 1	0.95	0.88	1	0.70	1.1
STD 1	0.95	0.85	1	0.65	1.0

*Denotes "LESS THAN" (Below detectable limit of procedure used).

TABLE IA

COMPARISON OF WASTEWATER ANALYSIS FOR FLUORIDE USING TEST KITS AND EPA APPROVED PROCEDURE WITH DISTILLATION

Sample	EPA Approved Procedure	Kit 2	Kit 5	Kit 6	Kit 7
1	1.34	2.92	2.33	2.16	2.33
2	405	405	350	280	400
3	1.57	1.80	1.2	1.02	2.0
4	0.68	1.96	0	0.09	2.7
5	36.4	63	0.28	43.4	84
6	20.4	66.0	24	42	96
7	15.3	16.68	9.6	18.0	9.0

TABLE i

KIT	ACCURACY		REPEATABILITY	EASE OF USE
	With Distillation	No Distillation		
2	6.2	3.5	9.9	7.0
5	4.5	1.0	10	9.0
6	1.0	2.8	9.8	7.0
7	2.3	2.6	9.6	9.0

TABLE J

COMPARISON OF WASTEWATER ANALYSIS FOR PH USING TEST KITS AND EPA APPROVED PROCEDURE

Sample	EPA Approved Procedure	Kit 1	Kit 3	Kit 5	Kit 6	Kit 7
1	8.0	7.8	7	7.0	6.90	8.0
2	12.6	10.0	11	10.5	**9.50	11.0
3	8.5	8.0	7	7.5	7.25	8.0
4	8.3	8.0	7	7.5	7.70	8.0
5	11.8	**10.0	11	10.5	**9.50	11.0
6	8.8	8.5	8	8.5	8.81	9.0
7	8.7	8.5	7	9.0	8.87	9.0
8	8.4	8.5	7	8.0	8.15	8.0
9	8.5	8.5	7	8.5	8.41	8.0
10	7.6	8.0	6	8.5	8.14	8.0
11	8.2	8.0	7	7.5	7.02	7.0
12	7.6	7.5	6	7.0	7.00	7.0
13	8.5	8.0	8	7.5	7.02	8.0
14	7.2	7.5	7	7.5	7.04	7.0
15	8.4	8.5	7	8.5	8.16	8.0
STD 4.0	4.0	4.0	5	*	*	4.0
STD 7.0	7.0	6.0	7	*7.0	6.6	7.0
STD 10.0	10.0	10.7	10	10.0	**10.0	11.0
STD 7	7.	6.0	7	*	6.6	7.0
STD 7	7.	6.0	7	*	6.6	7.0
STD 7	7.	6.0	7	*	6.6	7.0
STD 7	7.	6.0	7	*	6.6	7.0
STD 7	7.	6.0	7	*	6.6	7.0
STD 7	7.	6.0	7	*	6.6	7.0

*Denotes "LESS THAN" (Below detectable limit of procedure used).
**Denotes "GREATER THAN".

TABLE 1

KIT	ACCURACY	REPEATABILITY*	EASE OF USE
1	6.8	10	9.5
3	1.0	10	8.0
5	4.3	10	9.5
6	6.1	10	7.0
7	6.6	10	9.5

*EPA Approved Procedure rated at 10.

SUMMARY:

Numerous kits are available for monitoring regulated pollutant parameters on wastewater samples. The kits evaluated in this study frequently were unable to accurately analyze a wide variety of metal finishing discharges.

No one manufacturer provided kits that performed best on all parameters. It is apparent that the metal finisher must establish correlation between the analytical results obtained with the kits he uses and accepted EPA analytical procedures.

Furthermore, whenever possible, EPA approved sample preparation procedures must be followed prior to the use of a kit for quantification.

APPLICATION OF STATISTICAL PROCESS CONTROL TO WASTEWATER PRETREATMENT

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INTRODUCTION

With the increasing complexities of the EPA regulations and the inherent associated compliance costs, the need to apply statistical process control to manage the wastewater pretreatment operations in the metal finishing industry is more crucial now that it has ever been.

Statistical Process Control (SPC) is the monitoring of process variables quantitatively, and using statistical signals to stabilize it in order to accomplish a consistent predictable performance.

The implementation of statistical process control at Superior Metal Products involves five steps:

1. Written Process Control Procedure
2. Data Gathering
3. Process Control
4. Process Capability
5. Process Improvement

The starting point of SPC is the written process control procedure for the wastewater pretreatment operation (Fig. 1). This procedure serves as a master plan for the data gathering so that adequate, appropriate and accurate data are gathered. It outlines the process flow and the corresponding key variables that need to be controlled.

Establishing controls involves graphic display of data in control charts, analysis and corrective action to obtain consistency in the process. Without a consistent base from which to work, improvement actions are not effective.

Capability evaluation, which can occur only after control is established, assesses the process's ability to meet the pretreatment regulations.

After process capability is assessed, management decides upon a course of action relative to capability improvement. Other problem solving skills are frequently used in making this decision.

The main objective of this paper is to present the highlights of the success story behind the actual case history application of Statistical Process Control.

SUPERIOR METAL PRODUCTS	PROCESS CONTROL PROCEDURE WASTEWATER PRETREATMENT	ISSUED FEB. 1985 REVISED	
		FILE NUMBER WWT-1	PAGE NUMBER 1

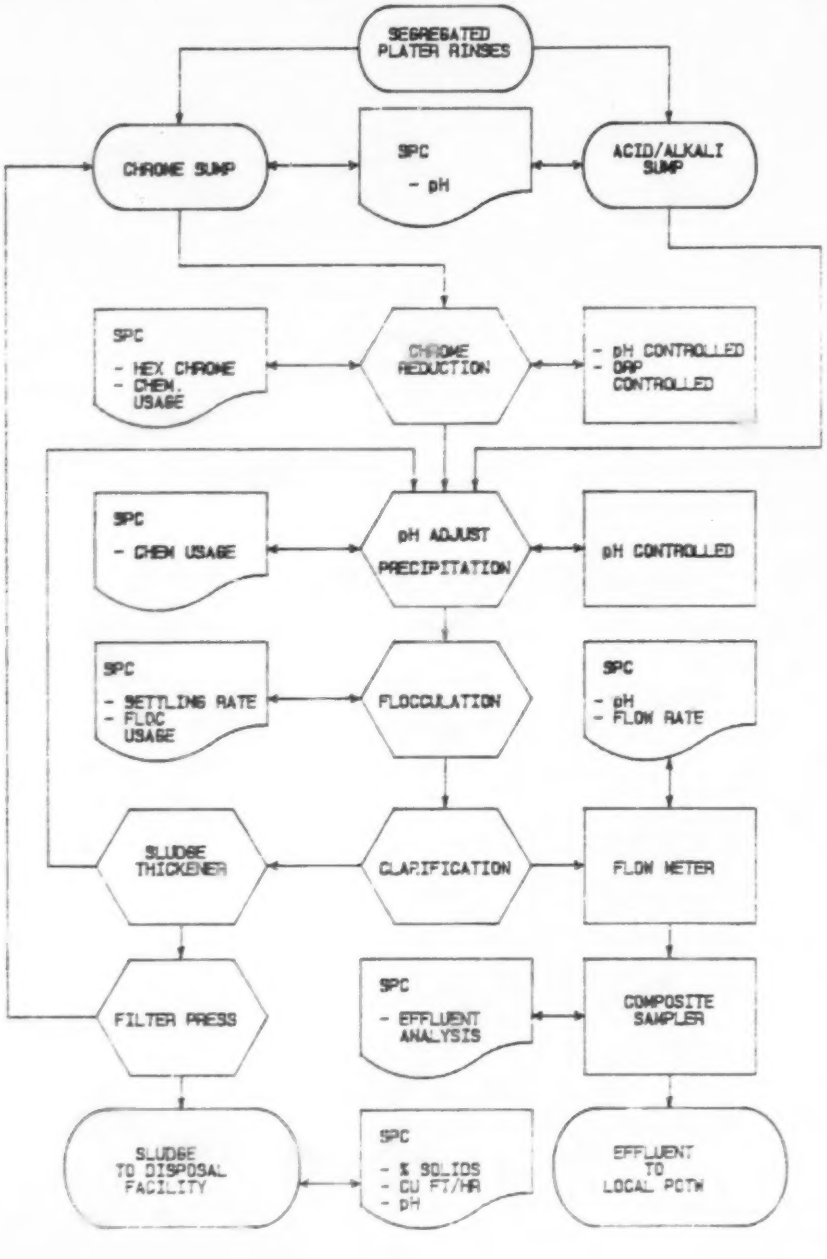

SEGREGATED PLATER RINSES
CHROME SUMP
SPC - pH
ACID/ALKALI SUMP
SPC - HEX CHROME - CHEM. USAGE
CHROME REDUCTION
- pH CONTROLLED - ORP CONTROLLED
SPC - CHEM USAGE
pH ADJUST PRECIPITATION
pH CONTROLLED
SPC - SETTLING RATE - FLOC USAGE
FLOCCULATION
SPC - pH - FLOW RATE
SLUDGE THICKENER
CLARIFICATION
FLOW METER
FILTER PRESS
SPC - EFFLUENT ANALYSIS
COMPOSITE SAMPLER
SLUDGE TO DISPOSAL FACILITY
SPC - % SOLIDS - CU FT/HR - pH
EFFLUENT TO LOCAL POTW

FIGURE 1

EPA COMPLIANCE

The ultimate goal of the application of statistical process control to wastewater pretreatment is the consistent compliance to the EPA standards. The following data on the analysis of chromium, nickel and total suspended solids gives a very good picture of the kind of process control and effluent quality improvement that can be expected using SPC as management tool.

BASELINE DATA

Figures 2, 3 and 4 show the baseline data on chrome, nickel and total suspended solids which covers the period from the start up of the pretreatment facility to the cut off date of the old EPA effluent standards, which was Part 413 Pretreatment Regulations published January 28, 1981 in Federal Register for discharge to Publicly Owned Treatment Works.

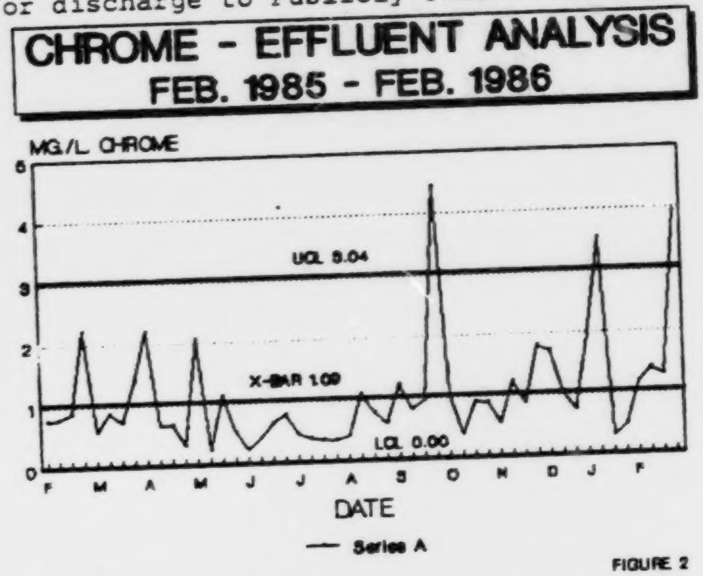


FIGURE 2

E.P.A. LIMIT = 7.00

The control chart for chrome (Fig. 2) shows that the upper control limit was 3.04 mg/l. Inspite of the fact that it was out of statistical control on three instances, there was however no violation because the old pretreatment standard of 7.00 mg/l was above the upper control limit of the process.

While the out of control conditions for chrome did not translate into any effluent standard violation, the story for nickel was different. In this particular case all the out of control conditions were also a non-compliance due to the fact that the EPA limit of 4.10 mg/l was lower than the process upper control limit of 4.84 mg/l (Fig.3 .

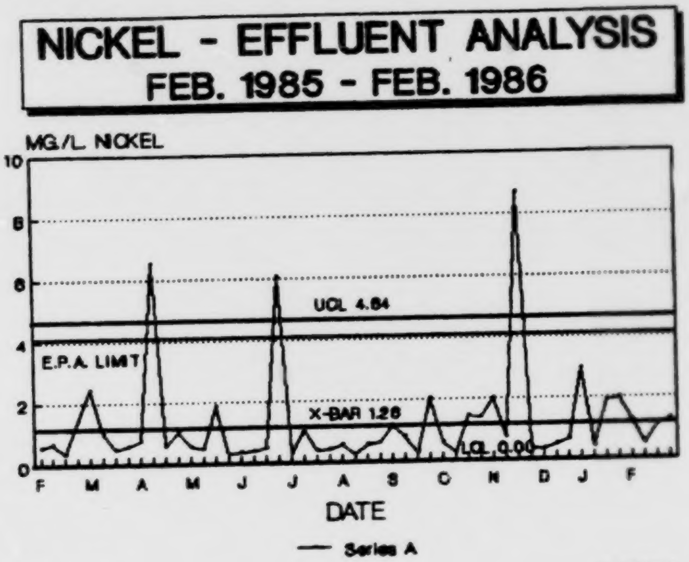


FIGURE 3

E.P.A. LIMIT = 4.10

Figure 4 shows the control chart for the total suspended solids.

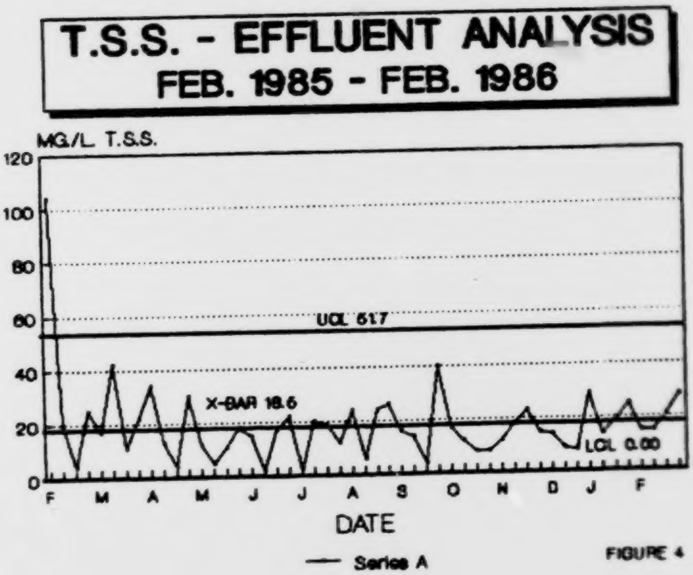


FIGURE 4

For the most part the baseline data represent the learning curve for the company in terms of understanding the wastewater pretreatment process. While no definite correlation between process variables has been established, assignable causes for the process variations has been identified and corrective actions were implemented to obtain consistency in the process performance.

At this point in time, it was obvious that process capability improvement was necessary if the process is to consistently meet the new Part 433 Pretreatment Regulations published July 15, 1983 for all metal finishing discharges with compliance date of February 15, 1986.

CURRENT DATA

The current data are presented in two sets of time frames:
Set I. March 1986 - December 1986
Set II. May 1986 - December 1986

During the months of March and April 1986 a significant process variation and corresponding assignable cause was identified. A very important correlation between the chrome, nickel and the total suspended solids was established. For this reason the May 1986-December 1986 data will be treated and discussed separately. It reflects the present status of the capability of the wastewater pretreatment process after the corresponding improvement was made part of the standard operation procedure.

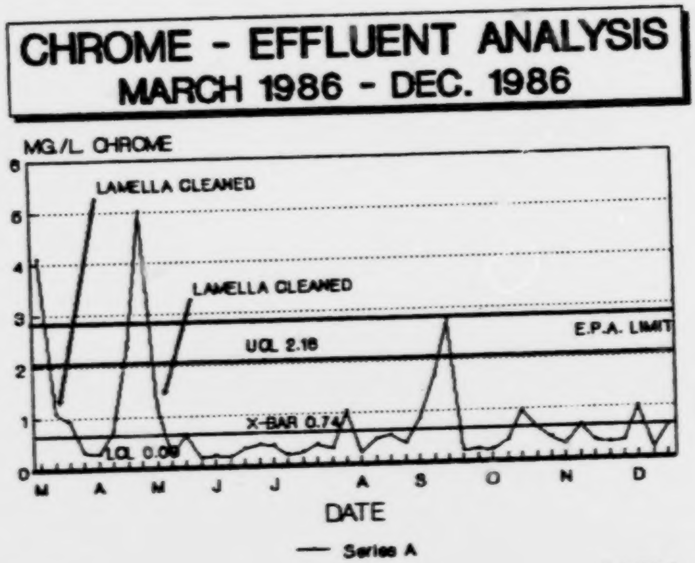
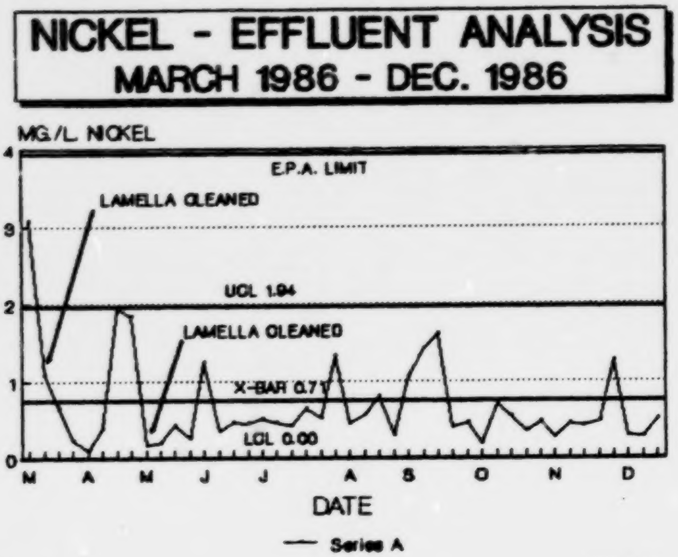
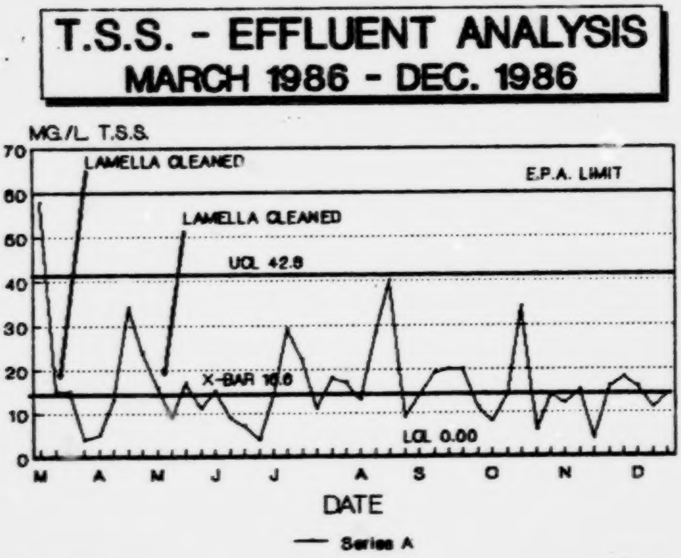


FIGURE 6

E.P.A. LIMIT - 2.77

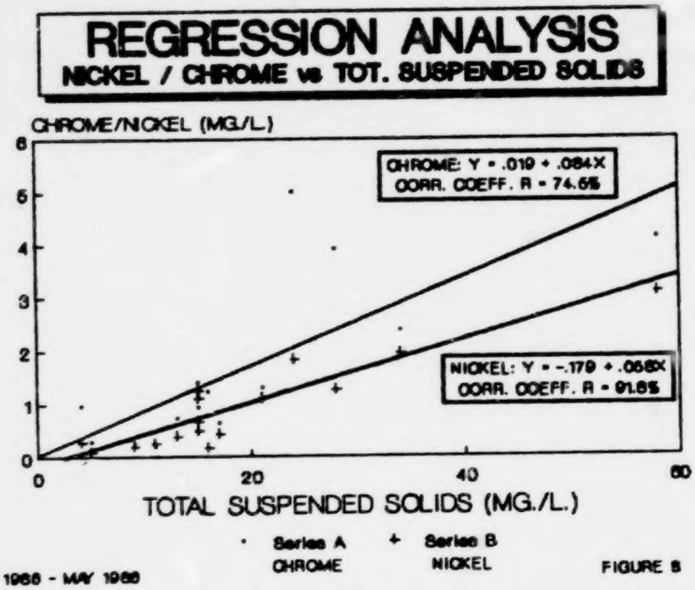


E.P.A. LIMIT 3.98 FIGURE 6



E.P.A. LIMIT - 60.0 FIGURE 7

Figures 5, 6 and 7 show the process control charts for chrome, nickel and total suspended solids for the period from March thru December 1986. A close visual comparsion of these charts reveals that during the month of March and April there was a very definite correlation between the peaks of these three parameters. This would indicate that the problem was caused by some solids floating out of the lamella gravity settler. The corrective action of cleaning the lamella to improve the settling efficiency was very effective in reducing the concentration of metal in the effluent. Regression analysis (Fig. B.) showed the correlation of the chrome and nickel concentration as a function of the total suspended solids which is described by the following equations:



FEB. 1988 - MAY 1988

FIGURE 8

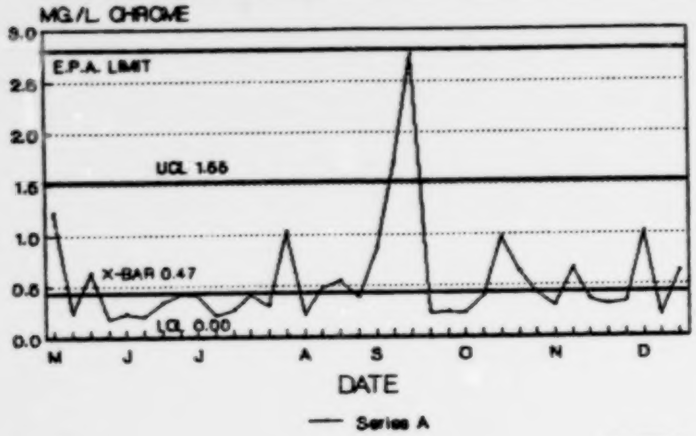
Chrome: Y = .019 + .084 X (Equation 1)

Nickel: Y = .179 + .058 X (Equation 2)

where X is the concentration of total suspeded solids. The correlation coefficient between chrome and total suspended solids was 74.5% while it was 91.8% between nickel and total suspended solids. The higher correlation for nickel is due to the fact that nickel hydroxide is lighter than chrome hydroxide as a precipitate and has therefore greater tendency to float.

Figure 9 and 10 are the most current control charts for chrome and nickel after the process improvement. The process is now capable of consistently maintaining an average concentration of 0.47 mg/l chrome and 0.59 mg/l nickel with an upper process control limit of 1.55 mg/l chrome and 1.58 mg/l nickel.

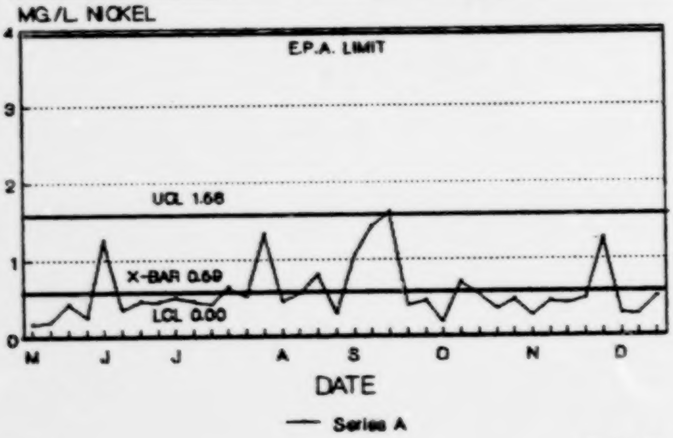
CHROME - EFFLUENT ANALYSIS
MAY 1986 - DEC. 1986



E.P.A. LIMIT 2.77

FIGURE 9

NICKEL - EFFLUENT ANALYSIS
MAY 1986 - DEC. 1986



E.P.A. LIMIT 3.98

FIGURE 10

PROCESS CAPABILITY

The following table summarizes the EPA compliance data of the wastewater pretreatment operation at Superior Metal Products:

Table 1: EPA Compliance Data

	X-Bar	UCL	EPA Limit	Process Capabiltiy
Chrome:				
Feb. 85 - Feb. 86	1.09	3.04	7.00	100.0%
Mar. 86 - Dec. 86	0.74	2.18	2.77	98.1%
May 86 - dec. 86	0.47	1.55	2.77	100.0%
Nickel:				
Feb. 85 - Feb. 86	1.26	4.84	4.10	96.0%
Mar. 86 - Dec. 86	0.71	1.94	3.98	100.0%
May 86 - Dec. 86	0.59	1.58	3.98	100.0%
Total Suspended Solids:				
Feb. 85 - Feb. 86	18.5	51.7	60.0	99.7%
Mar. 86 - Dec. 86	16.6	42.3	60.0	100.0%
May 86 - Dec. 86	15.6	37.5	60.0	100.0%

This summary table depicts a very good picture of the continuing process improvement that is taking place at the wastewater pretreatment operation at Superior Metal Products. With the help of Statistical Process Control the process is now capable of consistently producing an effluent quality level that contains less than 2.0 mg/l of either chrome or nickel, which in the early part of the project was said to be onlu posssible if a final polishing of the effluent is done using a sand filter.

SLUDGE REDUCTION

With the cost of sludge disposal increasing at a rapid rate coupled with the need to comply with the RCRA regulation for waste minimization, it has become a necessity to reduce the volumes of sludge generated during the pretreatment of the metal bearing wastewater. One way of achieving this objective is to control and improve the percentage of solids in the filter press cake using statistical process control.

Figure 11 shows the control chart for the per cent solids in the filter press cake. The base from which to work and make process improvement was the average 24.0% solids for the month of September 1985. After this base has been established, the recirculation of sludge from the bottom of the lamella back to

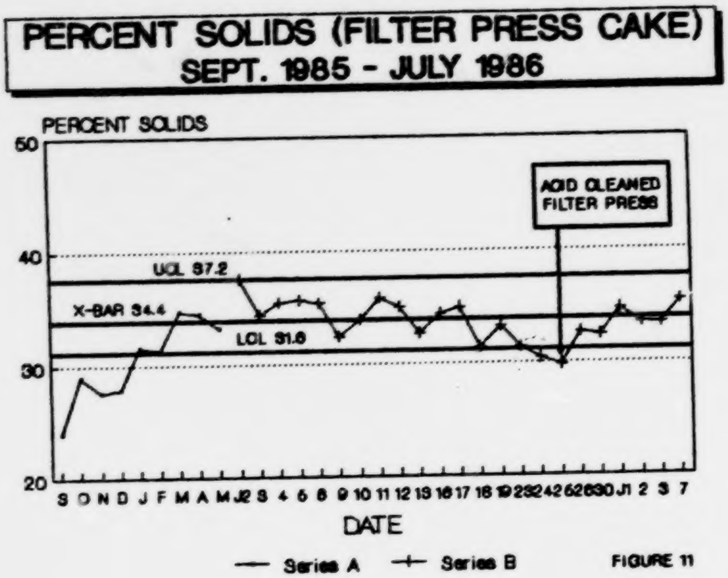


FIGURE 11

the neutralization tank was gradually increased while taking regular sampling of the filter press cake to determine the per cent solids.

Initial improvement was attained in October but tended to level off in the months of November and December. At this point further effort was made into increasing the recirculation of the sludge which resulted into another improvement in January and again leveling off thru the month of February. Then starting March after evaluation of the SPC data another process improvement was made through a system change in the recirculation loop of the sludge. The new system recirculates sludge from the bottom of the sludge concentrator back to the neutralization tank. The idea behind this approach is that the sludge at the concentrator has a higher solid consistency than the sludge at the lamella.

The process is now capable of producing a filter press cake that has an average of 34.4% solids with upper control limit of 37.2% and a lower control limit of 31.6%. The lower control limit is the control in place to determine when the filter press needs to be acid cleaned.

Figure 12 shows the control chart for the cubic feet of sludge generated per hour.

CUBIC FEET OF SLUDGE / HOUR
SEPT. 1985 - NOV. 1986

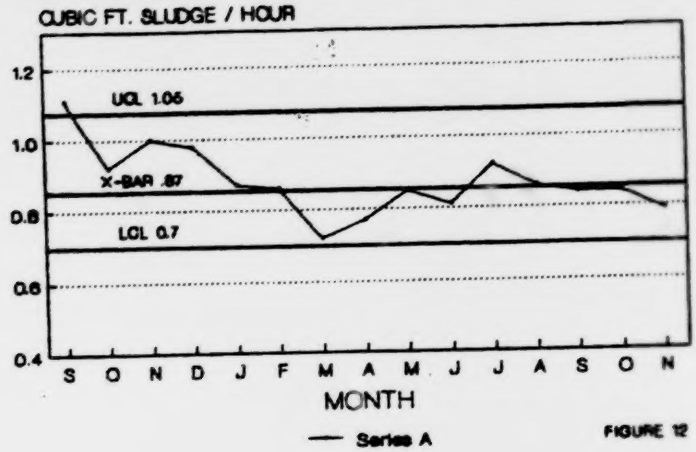
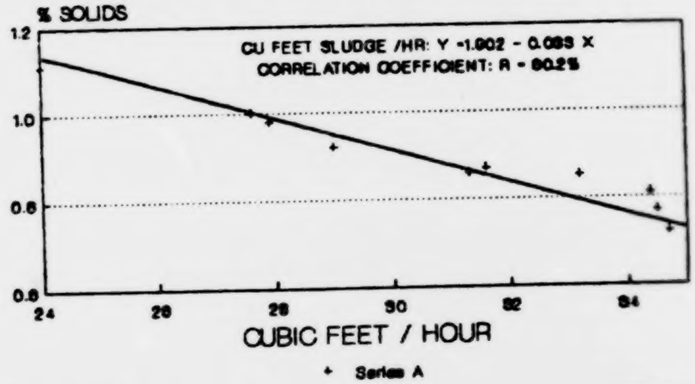


FIGURE 12

REGRESSION ANALYSIS
CUBIC FEET SLUDGE / HOUR vs
% SOLIDS (FILTER PRESS CAKE)



SEPT. 85 - JUNE 88

FIGURE 13

The regression analysis (fig. 13) showed the correlation between the per cent solids and the volume of sludge in cu. ft. per hour. The correlation coefficient is 80.2%.

The following table summarizes the process improvement relative to the effort to reduce the volumes of sludge.

Table 2

	Sept. 85	Nov. 86	% Change
% Solids	24.0	34.4	43.3%
Cu. Ft./Hr	1.11	0.79	28.8%

This SPC effort resulted in the reduction of the sludge volumes by 28.8%, an effort which enabled the company to go into a three shift operation without additional disposal cost.

WASTEWATER PRETREATMENT CHEMICAL COSTS

The chemical cost of treating the wastewater has always been the major concern in the metal finishing industry. In most cases, especially for small platers, this could mean the loss of competitive position, the loss of markt share and eventuallly going out of business. As a result, improving the quality of the effluent to meet a tighter EPA limit, is always a subject of protest. Just like in any other business operation, there is a common misconception that improving the quality of the product is tied up with higher cost.

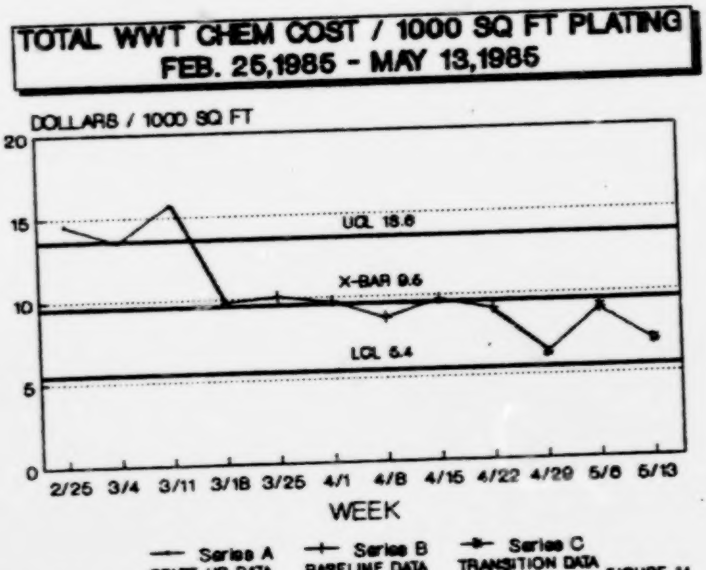


FIGURE 14

BEFORE POLYBLEND

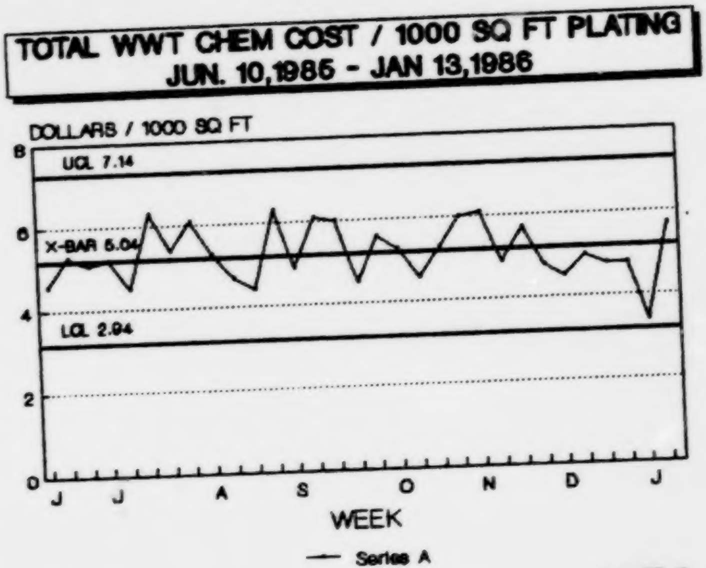


FIGURE 15

AFTER POLYBLEND

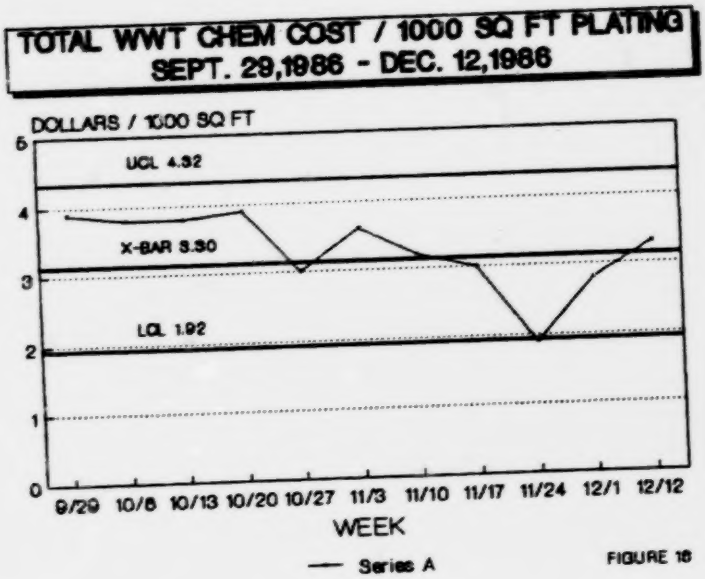


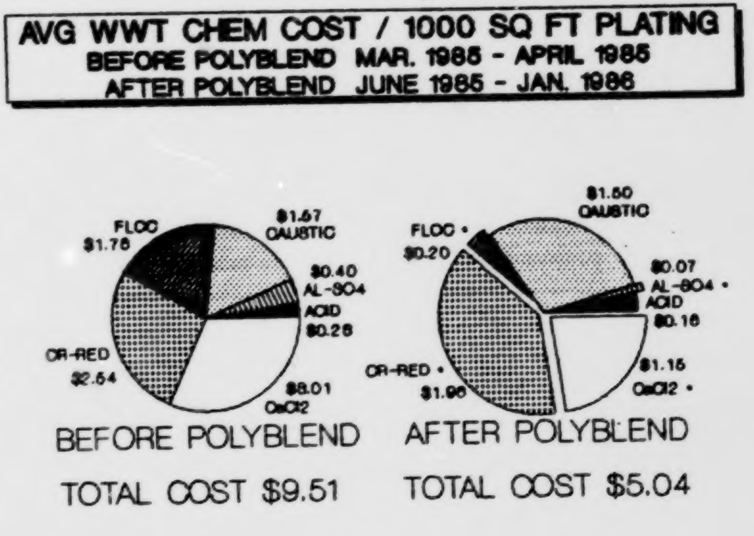
FIGURE 16

Figures 14, 15 and 16 show the control charts for the total wastewater treatment chemical cost covering the following periods:

1. Baseline Data (Before Polyblend): Feb. 85 - May 85
2. After Polyblend: June 85 - Jan. 86
3. Current Data: Sept. 86 - Dec. 86

The word polyblend has been used as a bench mark because after the start up of the pretreatment system, the cost of polymer was unreasonably high at an average of $1.76 per 1000 sq. ft. of plating. The obvious solution was the use of concentrated polymer which necessitated the use of the polyblend pumping system.

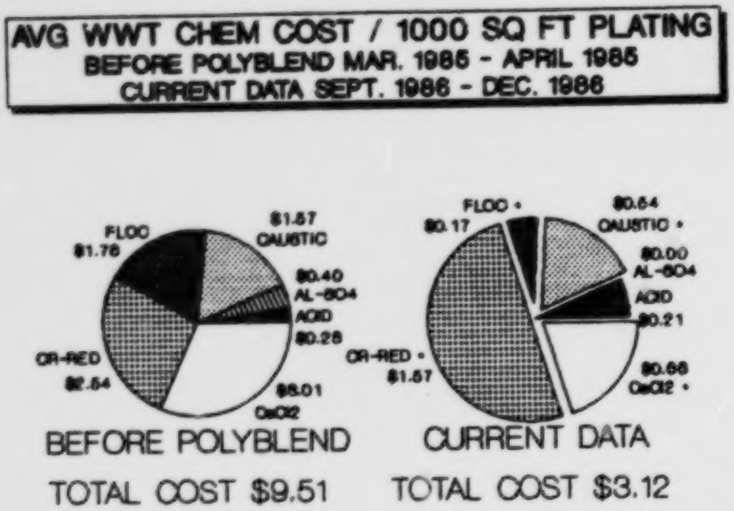
Figure 17 shows the pie charts comparing the costs before and after polyblend. The total cost before polyblend was $9.51 / 1000 sq. ft which was reduced to $5.04 / 1000 sq. ft of plating. The major factors in this cost reduction were the costs of polymer, chrome reducer, calcium chloride and aluminum sulfate. In terms of percent the most dramatic reduction was in the polymer usage, while the biggest dollar impact came from the reduction in the cost of calcium chloride.



• MAJOR FACTORS IN COST REDUCTION

FIGURE 17

Figure 18 shows the current costs compared to the costs before the polyblend.



* MAJOR FACTORS IN COST REDUCTION

FIGURE 18

The use of concentrated polymer in conjunction with the polyblend was primarily responsible for the reduction in the cost of flocculation, while controlling the process through synchronization of the wastewater flow from the chrome sump with the flow from the acid/alkali sump resulted in the reduction of the other chemical costs.

The following table is the summary of the wastewater pretreatment chemical costs per 1000 sq. ft. of plating:

Table 3

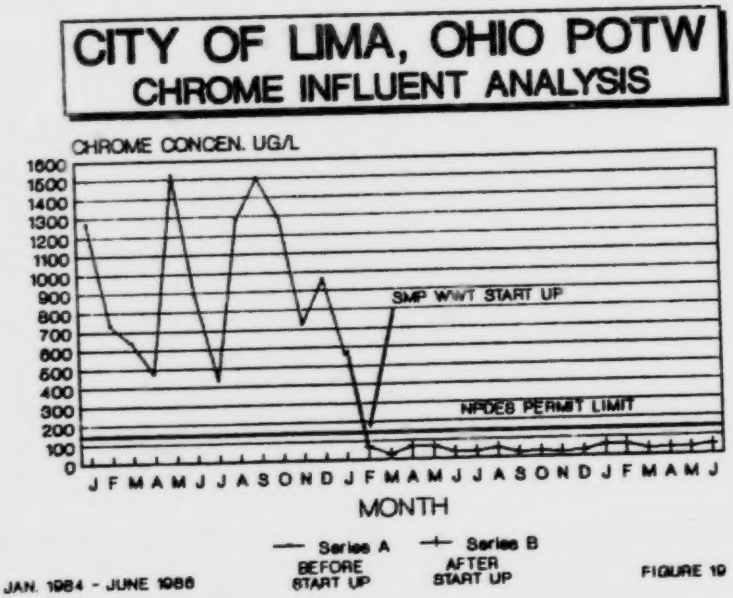
	Before Polyblend	After Polyblend	Current Data
Floc	$1.76	$0.20	$0.17
Caustic Soda	$1.57	$1.50	$0.54
Aluminum Sulfate	$0.40	$0.07	-----
Acid	$0.23	$0.16	$0.21
Calcium Chloride	$3.01	$1.15	$0.63
Chrome Reducer	$2.54	$1.96	$1.57
Total	$9.51	$5.04	$3.12

In the previous part of this paper, it was shown that statistical process control has helped improved the quality of the effluent. In this section, it was shown that the application of the same management tool resulted in the reduction of chemical cost.

As part of the continuing improvement through the use of SPC, a new chemical cost reduction project involving the chrome reducer has been lined up for 1987. It is expected that with the use of a counter spray rinsed and the atmospheric evaporator, the drag out loss of the chrome plating solution can be reduced by 80%. This will result in corresponding reduction in the cost of chrome reducer. The combined savings estimated at around $45,000.

IMPACT ON THE LOCAL POTW

Figure 19 and 20 show the impact of the wastewater pretreatment operation of Superior Metal Products on the quality of the influent to the City of Lima Wastewater Treatment Plant. Prior to the start up of the pretreatment facility, the chrome and nickel concentration in influent was very high. After the company started pretreating its wastewater, the concentration of these two metals in the influent to the city POTW is already below the NPDES regulation so that in theory it could be discharge without treatment if those were the only requirements.



JAN. 1984 - JUNE 1986

FIGURE 19

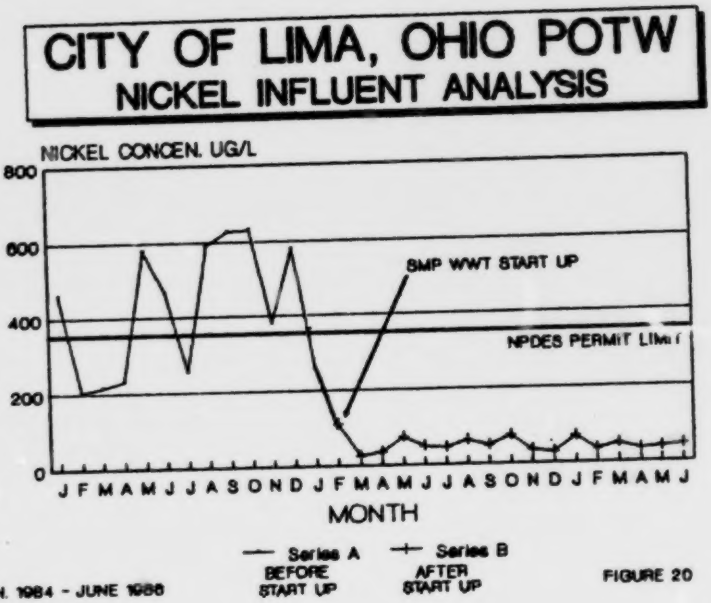


FIGURE 20

SUMMARY AND CONCLUSION

Today there is wide agreement that continual improvement in quality and cost is not only possible but also realistic and necessary. This paper has shown that those goals may be pursued in concert, that they are not in opposition. The key is the application of Statistical Process Control (SPC) to manage a business operation or a process.

The following are the benefits derived from the use of SPC in Wastewater pretreatment:

For the company, it triggers a positive chain reaction involving: better understanding of the process, better effluent quality, EPA compliance, lower cost, stronger competitive position, and greater market share.

For the community, the better quality of the effluent from the pretreatment facility translates into better quality of the influent to the local POTW (Publicly Owned Treatment Works) which would mean less treatment cost.

For the society at large, it means a better and healthier environment.

WASTE WATER REDUCTION IN METAL FABRICATIONS OPERATIONS

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Abstract

The Savannah River Plant produces special nuclear materials for the U. S. Government. Since 1958, chemical wastes generated by an aluminum forming/metal finishing process used to manufacture fuel and target assemblies were discharged to a settling basin. This process waste stream contained acids, hydroxides, metal oxides, and chlorinated degreasing solvents. In 1981, trichloroethylene and tetrachloroethylene were discovered in monitoring wells near the settling basin. In November 1983, a federal law mandated that discharges to the basin be stopped within two years. A remedial action program to remove the solvents from the ground water and to close the settling basin was promptly implemented. Installation of a waste water treatment facility was required before basin closure. This required an accelerated program of process development to provide basic data for design.

Waste water from 87 process effluents totaled 528 gpm. A high spot venture guidance appraisal indicated that each gallon per minute reduction in waste water flow would reduce the capital cost of the treatment facility by $10,000. An engineering consulting firm was quickly selected, and their laboratory was assembled on site for an effluent characterization and flow reduction study. Composition of spent process solutions as well as drag out from each process solution to rinse water were then measured. Optimum combinations of counterflow rinse tanks with static rinses and rinsewater reuse where practical were determined for each production operation. In addition, a quench water treatment system was developed to remove emulsified oil and carbon and to recycle the effluent of that unit operation. The study indicated that inplant modifications could greatly reduce the total waste water effluent, thus reducing the size of the waste water treatment facility and reducing overall program costs. A composite sample of the projected wastewater after flow reductions was used in treatability tests to develop the flowsheet for the treatment facility and to provide basic data for its design. The waste water flow reduction to 20 gpm was achieved, and the treatment facility was successfully started up in July 1985.

Source of M-Area Wastewater

Fuel and target assemblies for the nuclear reactors of the Savannah River Plant are fabricated in 300-M Area which has three production buildings and two support laboratories. In two of these buildings, uranium and lithium alloys of aluminum are cast, extruded and drawn into long tubes with aluminum cladding. In the other building, short tubular shaped uranium cores are nickel plated and clad in aluminum cans by hot die size bonding. Production lines and equipment that are major sources of wastewater are shown in Table 1.

Uranium cores, that have been pre-etched in nitric, phosphoric and hydrochloric acids, are nickel plated in a Watts bath. Aluminum tubes, caps and cans are cleaned by degreasing in 1,1,1-trichloroethane, etching in caustic, desmuting in nitric acid and surface treating in phosphoric acid. After aluminum forming operations, quench water cools product. Finished product is tested in steam autoclaves, and wastewater from failures contains uranium, nickel and aluminum oxide particles. Some uranium cores are recovered from rejected product by stripping of aluminum and nickel cladding in caustic and nitric acid etch tanks. Air exhaust from hot nitric acid tanks is scrubbed by water in a two stage dimester. Aluminum forming tools are degreased in 1,1,1-trichloroethane and etched in caustic.

All quench and rinse tanks in the original M-Area production buildings were single stage, once through operations. Process water was supplied from wells and wastewater was discharged to a basin.

Table 1. 300-M AREA WASTE WATER

THREE PRODUCTION BUILDINGS & TWO LABORATORIES

ONE	NICKEL PLATING LINE
FIVE	ALUMINUM CLEANING LINES
TWO	SLUG QUENCH OPERATIONS
ONE	URANIUM SLUG AUTOCLAVE TEST FACILITY
ONE	ALUMINUM/NICKEL STRIPPING LINE
ONE	ACID SCRUBBER STACK
ONE	TOOL CLEANING LINE

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Initial Effluent Assessment

Two hundred and fifty separate effluents into the M-Area process sewer were identified. Discharge routes to the sewer were confirmed by adding dye at each source. An orifice was installed in the supply line to production buildings, and effluent flows were measured by closing each inlet valve and observing the pressure differential. Quench and rinsewater flows were more accurately determined with the supply valves at normal settings by draining each tank, closing the large drain valves, and measuring the rate of level increase. Noncontact cooling water and steam condensate, which discharged to the process sewer and mix with wastewater, were clean waters that did not require treatment and were rerouted to the storm sewer. The remaining wastewater from 87 process effluents totaled 528 gpm.

The chemical composition of spent solution from the 22 process tanks was first estimated by analysis of metal concentration and stoichiometric calculations. The average composition of combined M-Area wastewater was then estimated from discharge records of the solution control operators for a selected reference year. The estimated discharge was checked by material balance of raw chemical consumption from purchase records, which indicated it to be 85 to 92% accurate.

Spent solution in each process tank was collected just before discharge, and sample volumes proportional to the estimated annual discharge were used to make up a composite of M-Area wastewater. Bench scale treatability tests with the composite sample indicated that, after pretreatment for uranium removal, EPA effluent guidelines for the Aluminum Forming and Metal Finishing Industries could be achieved by hydroxide precipitation, Best Available Technology Economically Achievable (BAT). A high spot venture guidance appraisal for both 100 and 250 gpm wastewater treatment facilities revealed that construction cost would be lowered by $10,000 for each gallon per minute reduction in wastewater flow.

Effluent Characterization/Flow Reduction Study

An engineering consulting firm was then selected for a detailed M-Area Wastewater Characterization/Flow Reduction Study. A laboratory was placed on site to expedite this program.

During this study samples were collected from the process sewer of each production building and laboratory for complete priority pollutant analysis to ensure that all chemicals being discharged were known. (This revealed one pollutant which was not even known by the chemical supplier.) Then samples of spent concentrated solution were collected from each process tank just before three normal discharges, and analyzed for known chemicals. The solution was first circulated using a portable pump with flexible hose to ensure good agitation of the larger tanks, which are long and narrow. Smaller tanks were agitated with a paddle.

Rinsewater Flow Reduction

Dragout of solution on racks and baskets from each process tank to a clean stagnant rinse tank was determined by measuring the concentration increase of metals, anions, and conductivity. Care was taken to duplicate movement of baskets and racks at the rate normally processed. Total volume of dragout per shift was then calculated. Greater than 95% accuracy was indicated by a material balance with chemicals purchased during a separate reference year of operation than the initial effluent assessment. The material balance for each production line in the independent reference years were also in good agreement when corrected for surface area processed.

Using these discharge and drag out measurments, production lines were studied for the optimum combination of counter flow and stagnant rinse tanks with rinsewater reuse where feasible. A high spot estimate for each proposed modification, including cost of the production line shutdown, was compared to the $10,000 saving in construction of wastewater treatment facilities for each gallon per minute flow reduction that modification would achieve. Space for inplant modification was limited, so only one or two additional rinse tanks per production line could be economically added. The cap-can aluminum cleaning line shown in Figure 1 is an example of the BEFORE and AFTER tank arrangement and

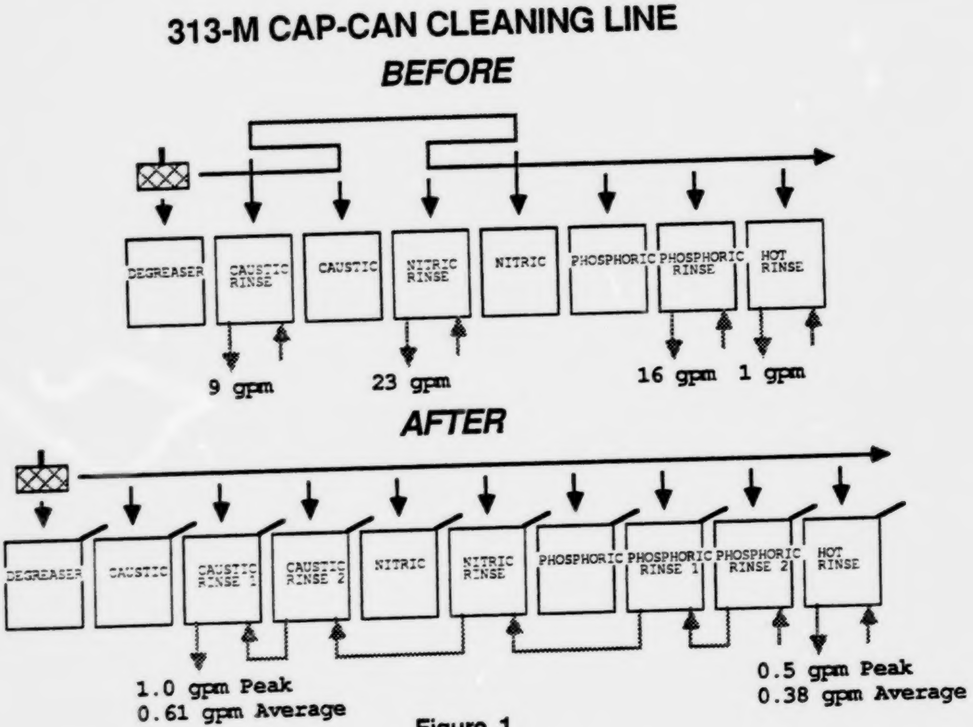

313-M CAP-CAN CLEANING LINE
BEFORE
DEGREASER
CAUSTIC RINSE
CAUSTIC
NITRIC RINSE
NITRIC
PHOSPHORIC
PHOSPHORIC RINSE
HOT RINSE
9 gpm
23 gpm
16 gpm
1 gpm
AFTER
DEGREASER
CAUSTIC
CAUSTIC RINSE 1
CAUSTIC RINSE 2
NITRIC
NITRIC RINSE
PHOSPHORIC
PHOSPHORIC RINSE 1
PHOSPHORIC RINSE 2
HOT RINSE
1.0 gpm Peak
0.61 gpm Average
0.5 gpm Peak
0.38 gpm Average

Figure 1

rinsewater flow. Note that tanks were rearranged so that baskets move continuously through the line. There is now no cross drippage from reverse movement and drip boards were placed between tanks. Two counterflow rinse tanks were added, and rinsewater is now reused. The last tank in each production line is once-through rinse water flow, controlled separately to ensure the extra clean product required for nuclear reactors.

The maximum dragout concentration in rinse tanks that would produce acceptable product in the aluminum cleaning lines and especially in the plating line required experienced judgement by plant technical personnel and the contracted consultant. Data published in Technology Transfer Reports of EPA Industrial Environmental Research Laboratory also proved useful and accurate. Several arrangements and combinations of rinse tanks for each line were assessed for minimum rinsewater flow as well as minimum spent process solution discharge. The theoretical reduction from installation of a second rinse tank for two stage, counter-flow rinsing at ten locations is shown in Table 2 (see equation below table for method of calculation). To demonstrate that acceptable product quality could be achieved with proposed modifications, existing rinse tanks were seeded with process solution to the highest dragout concentration that would occur. Quality of product processed during these tests was measured by metallography and was acceptable.

Movement of product through the production lines may stop during shift change, lunch and breaks. As shown in Figure 2, a conductivity meter was installed in the discharge rinse tank to ensure minimum rinsewater effluent. Movement of the overhead hoist to above the first rinse tank in the production line now starts air agitation of all rinse tanks. Low conductivity in rinsewater effluent stops the air agitation and closes the rinsewater supply valve. High conductivity opens the rinsewater supply valve. Peak rinsewater flow is set manually using a rotometer in the supply line, and the volume of rinsewater discharged each shift is indicated by a flow totalizer. Timers, rather than conductivity meters, were installed to reduce rinsewater effluent from infrequently used tanks (viz. tool cleaning). Rinsewater flow remains on if a conductivity probe or timer fails, so that product quality is not affected. The failure is indicated by excess volume of rinsewater on the flow totalizer.

As shown in Table 3, the study indicated that inplant modifications would reduce the total rinsewater flow from 428 to 11 gpm (average flow during an 8 hour shift). The reduction from 54 gpm peak flow to 11 gpm shift average was achieved by the rinsewater conductivity meters and timers. Samples of spent process solution collected during the flow reduction study were then used to make a composite sample of the projected combined M-Area wastewater after flow reduction. These samples were then used in pilot treatability tests that provided basic data for design.

Table 2. SINGLE VS. COUNTERCURRENT FLOW TANK

BUILDING	PROCESS	TANK	THEORETICAL FLOW,GPM 1 TANK	2 TANKS
313-M	PLATING	PRE ETCH	22.4	1.0
		POST ETCH	159.5	1.5
	RECOVERY	CAUSTIC	12.0	0.5
		NITRIC	12.0	0.5
	CAP-CAN	CAUSTIC	13.0	0.5
		PHOSPHORIC	7.9	0.5
	FINAL ETCH	NITRIC	80.3	1.0
321-M	TUBE	NITRIC	56.0	1.0
	COMPONENT	NITRIC	132.0	1.5
		PHOSPHORIC	12.8	0.5

CALCULATION

$$Q = D\,(Co/Ce)^{1/n}$$

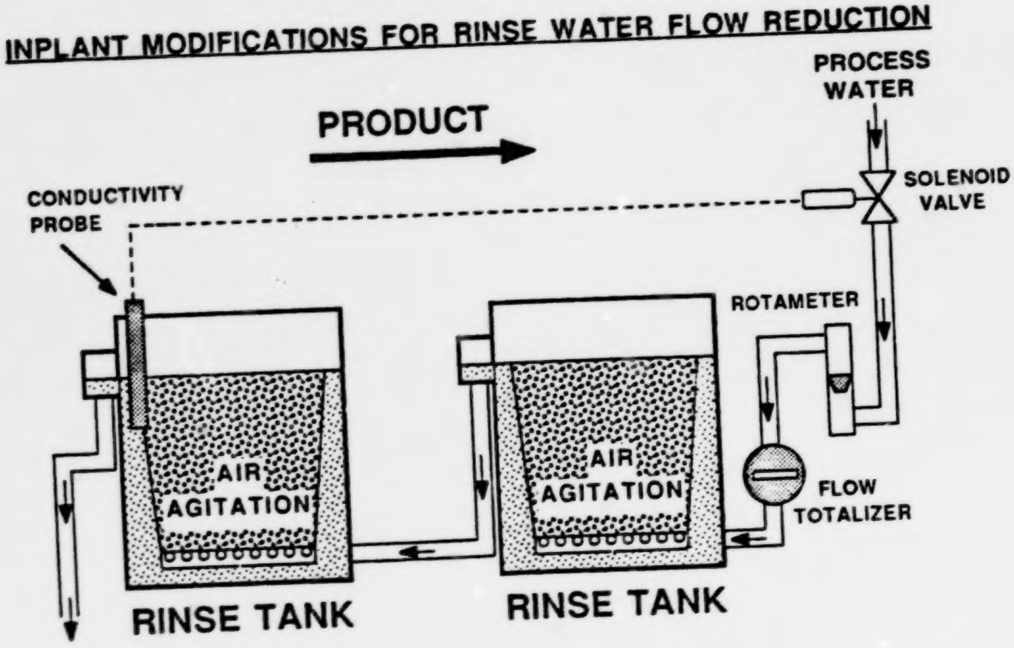
Q = Flow in rinse tank, gpm

D = Dragout of process solution, gpm

Co = Concentration in process tank, mg/l

Ce = Concentration in rinse tank, mg/l

n = Number of counter flow rinse tanks


INPLANT MODIFICATIONS FOR RINSE WATER FLOW REDUCTION

PROCESS WATER
PRODUCT
SOLENOID VALVE
CONDUCTIVITY PROBE
ROTAMETER
AIR AGITATION
AIR AGITATION
FLOW TOTALIZER
RINSE TANK
RINSE TANK

Figure 2

Table 3. RINSEWATER EFFLUENT FLOW RATES

		RECOMMENDED, GPM	
	1983,GPM	PEAK	SHIFT AVG.
313-M			
CAP-CAN	63	1.5	1.0
PLATING	49	9.0	4.4
RECOVERY	35	1.0	0.6
FINAL SLUG	26	1.0	0.2
TOOL	5	1.0	0.1
320-M			
CLEAN ROOM	25	25	0.2
321-M			
TUBE	157	6.0	3.5
COMPONENT	60	1.0	0.6
ASSEMBLY	8	7.5	0.4
TOTAL	428	54	11

Quench Water Recycle System

The flow reduction study recommended that a 60 gpm quench water effluent be treated and recycled by inplant modifications. During hot die size bonding of aluminum, hot product is dipped in a quench water tank and also sprayed with quench water. These quench water effluents drain to a collection sump into which hydraulic oil may also leak. This wastewater contains oil, colloidal carbon, aluminum oxide/mineral oil lubricant, and aluminum chips. Removal of these contaminants is necessary, because oil recycled through quench water spray nozzles will form an emulsion that is difficult to separate. In addition, carbon and aluminum particles will plug the spray nozzles.

Benchscale treatability tests revealed that removal of contaminants from the quench water would not be easy. When decantation was simulated, the aluminum oxide/mineral oil lubricant formed a third phase between the oil-water interface and sludge settled to the bottom. However, these tests indicated that residual oil and solids could be filtered using cellulose fiber media and filter aid. A pilot decanter and pressure filter were constructed to test the separation and provide basic data for design. After several modifications, greater than 90% oil and solids removal was demonstrated. Data indicated that recycle through the filter would attain the desired separation.

A schematic of the system that was developed, the Quench Water Recycle System, is shown in Figure 3. Quench water from the collection sump is pumped through a bag filter which removes aluminum chips that are salvaged. The water then slowly flows through a two stage decanter from which floating oil, including the aluminum oxide/mineral oil lubricant, is removed by adhesion to a rotating disk with scraper. The waste oil drains from the scraper to drums for transport to the power house where it is burned. Decanted water spills into a filter feed reservoir from where it is pumped to the pressure filter. Filter aid is added through a static inline mixer at the filter inlet. Filtrate drains into a clean reservoir and 90% is recycled to the feed reservoir by a flow control weir. The remaining filtrate is pumped from the clean reservoir through a heat exchanger to the quench tank and spray nozzles.

The rate of quench water evaporation changes as process conditions in the quench stations change (viz. production rate or product size). To maintain a constant volume of quench water in the system, a level controller was installed in the filter feed reservoir which adds process water or discharges filtrate as needed. Steam condensate is used for makeup of the filter aid solution to prevent salt accumulation in the quench water. The filter feed reservoir is sized to contain the largest potential spill of hydraulic oil into the quench station collection sump. A small floating decanter in this chamber continuously returns any residual oil on the surface to the inlet of the primary two stage decanter. The floating decanter is also used to quickly drum spilled oil.

QUENCH WATER RECYCLE SYSTEM

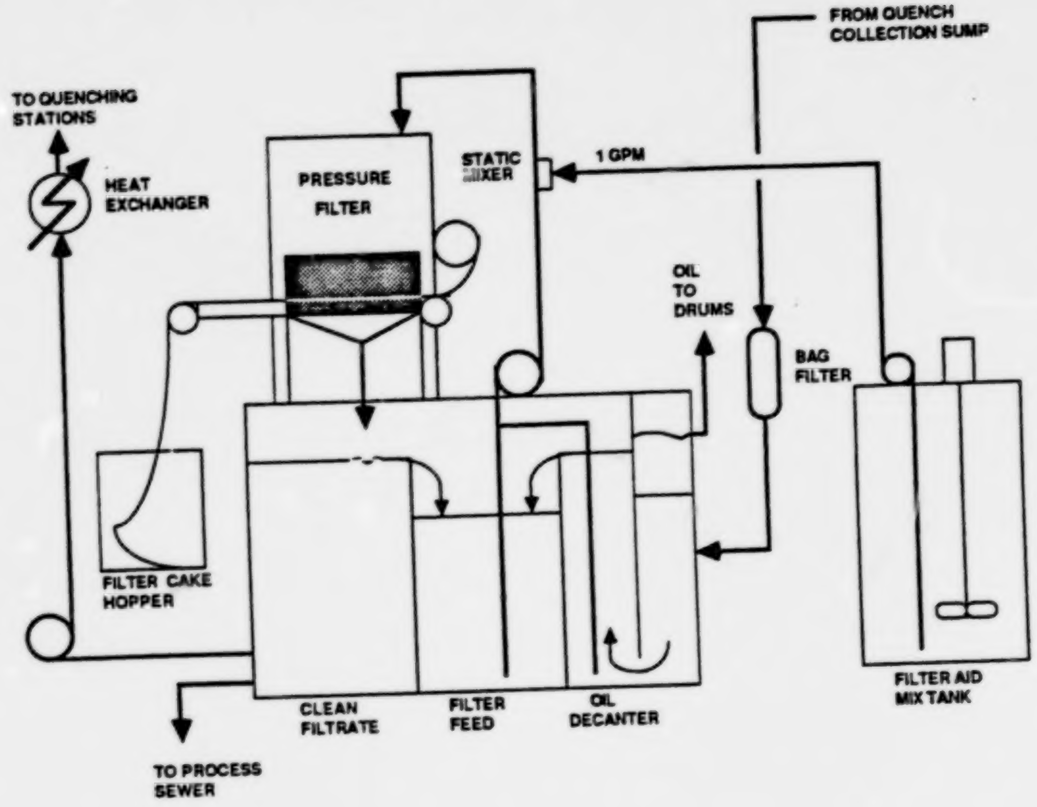

FROM QUENCH
COLLECTION SUMP
TO QUENCHING
STATIONS
HEAT
EXCHANGER
PRESSURE
FILTER
STATIC
MIXER
1 GPM
OIL
TO
DRUMS
BAG
FILTER
FILTER CAKE
HOPPER
CLEAN
FILTRATE
FILTER
FEED
OIL
DECANTER
FILTER AID
MIX TANK
TO PROCESS
SEWER

Figure 3

A sketch of the pressure filter is shown in Figure 4. This is a fully automated Oberlin Model HB with 7 square feet of filter area. Wastewater is distributed onto the media in a horizontal upper platen. When the differential pressure through the filter increases to 30 psig, the inlet valve closes ending the feed cycle. During the index cycle, the filtercake is dried with pressurized air, and the cake and media are automatically discharged into a hopper as clean media is drawn from a roll into the filter. At the end of each filter feed cycle sludge is pumped from the bottom of the oil decanter into the filter. During the index cycle, filter aid solution is circulated to the makeup tank to prevent pipe pluggage.

After system startup, oil removal efficiency was much better than expected; however, carbon particles accumulated in the quench water. Addition of diatomaceous earth to the cellulose fiber filter aid corrected this problem. Effective removal of the carbon and residual oil from quench water was then achieved. The discharged filtercake and media are suitable for incineration.

PRESSURE FILTER

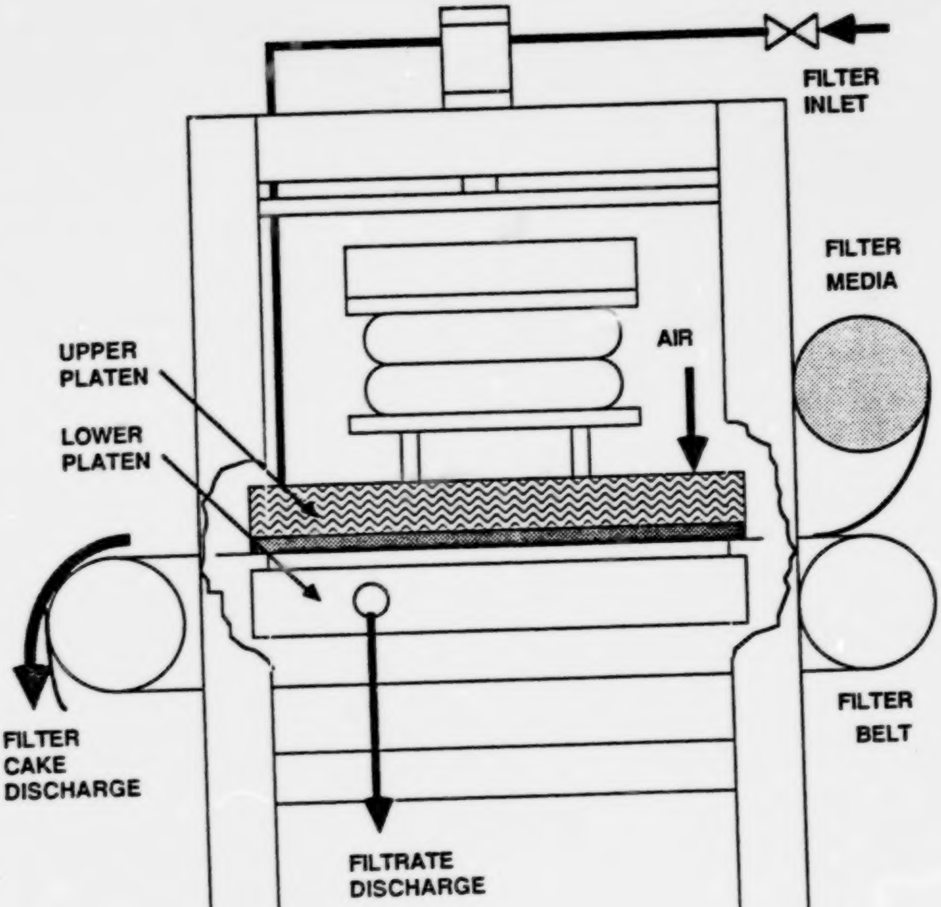

FILTER INLET
FILTER MEDIA
AIR
UPPER PLATEN
LOWER PLATEN
FILTER CAKE DISCHARGE
FILTER BELT
FILTRATE DISCHARGE

Figure 4

Stack Scrubber Recycle System

The exhaust air from the hoods of hot nitric acid tanks is scrubbed before discharge to stack. Water is sprayed onto demister pads in this two stage scrubber. Plans are to reduce the 9 gpm effluent from the scrubber to 1 gpm by installation of a recycle system with a collection tank and circulation pump, as shown in Figure 5. The scrubber operates at atmospheric pressure, so acid concentration in recycled water can increase to 10% wt HNO_3 without increasing NO_x gas emissions from the stack.

Other Flow Reduction Devices

As shown in Figure 6, all drains from production line sumps were sealed for spill control. Hose nozzles with automatic shutoff are now used to reduce the volume of floor flush water from housekeeping. Before pumping wastewater from the sumps, the pH is measured to ensure that process leaks are quickly detected. Separate sumps were installed for degreasers and 1,1,1-trichloroethane concentration is analyzed to ensure that no liquid solvent is in the sump before pumping to the process sewer.

Spring operated foot valves were installed on some laboratory sinks to reduce wastewater.

Flumes were installed in the process sewer from each production building, and flow is continuously recorded to monitor performance. This proved to be a very important administrative control tool for achieving flow reduction.

Basic Data For Design

The flow reduction study indicated that the combined wastewater from production buildings and laboratories could be reduced from 528 to 20 gpm by inplant modifications. Due to the accelerated schedule, all reductions could not be demonstrated before design of the treatment facility began; so the facility was sized for an average wastewater flow of 40 gpm, allowing a design safety factor of 2.

Flow Reductions Achieved

The Dilute Effluent Treatment Facility (DETF) was successfully started up in July 1985. As shown in Figure 7, the inplant modifications successfully reduced the average wastewater flow to 20-25 gpm. All of the recommended rinsewater flows shown in Table 3 were achieved with no loss of product quality. Only the volume and chemical concentration of wastewater from the spill control sumps of production lines exceeded projections.

During startup of each modified production line, technical surveillance ensured that product quality was maintained while the recommended flow reductions were attained. Problems initially thought to be caused by

313-M STACK SCRUBBER

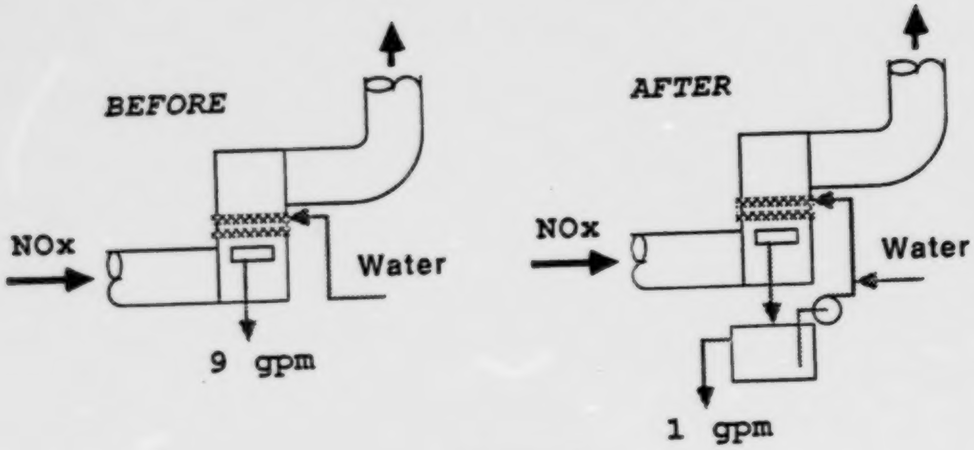

BEFORE
NOx
Water
9 gpm
AFTER
NOx
Water
1 gpm

Figure 5

FLOOR SUMPS

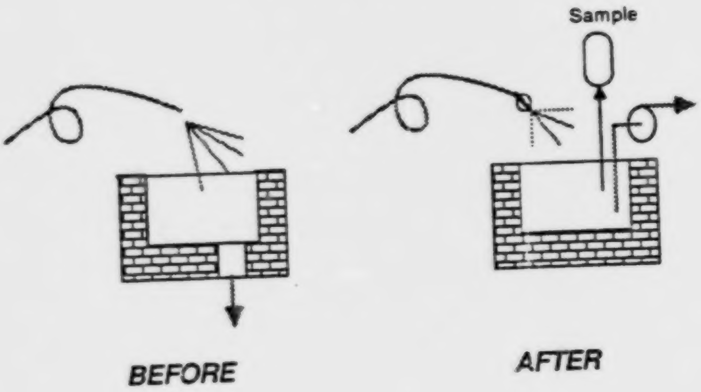

Sample
BEFORE
AFTER

Figure 6

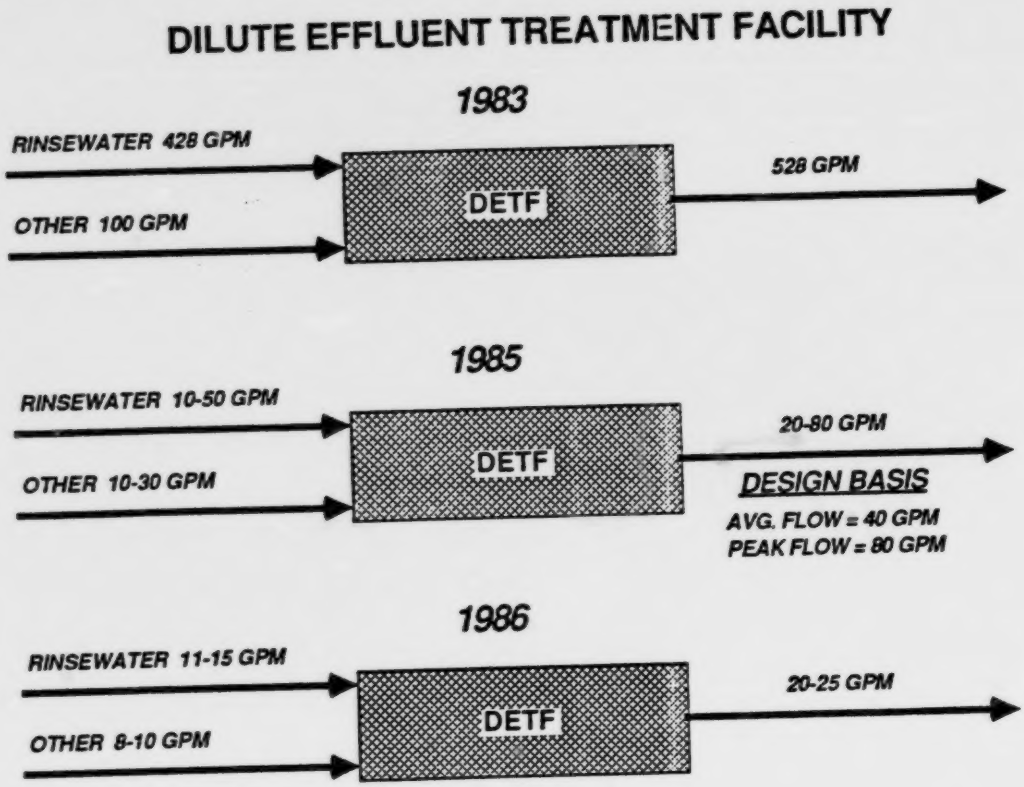

DILUTE EFFLUENT TREATMENT FACILITY
1983
RINSEWATER 428 GPM
OTHER 100 GPM
DETF
528 GPM
1985
RINSEWATER 10-50 GPM
OTHER 10-30 GPM
DETF
20-80 GPM
DESIGN BASIS
AVG. FLOW = 40 GPM
PEAK FLOW = 80 GPM
1986
RINSEWATER 11-15 GPM
OTHER 8-10 GPM
DETF
20-25 GPM

Figure 7

rinsewater flow reductions were quickly diagnosed as mechanical and were corrected. For example, smaller operators could not quickly move heavy baskets from caustic etch to rinsewater in the cap-can cleaning line due to a bend in the hoists monorail. The caustic etch and rinse tanks were relocated, and all shifts then produced clean cans at the reduced rinsewater flow.

Optimum techniques for handling of racks and baskets were determined by observing operators and correlating techniques with product quality. Past practice of not completely draining tubes before movement or splashing process solution into rinsewater when emptying etched cans were habits that some operators found difficult to change. Training emphasized the importance of allowing racks and baskets to drain before movement. Product was dripped three times in each rinse tank before inplant modifications. After modification, product was dipped twice in the first and once in the second counterflow rinse tank of lines with high production rates. Thereby, time for operators to process product did not significantly increase and peak production rates were achieved.

Cost Savings

As shown in Table 4, the net savings in construction cost by M-Area wastewater flow reduction was $1.5 million. Installation of flow limiting orificies had indicated that the combined M-Area wastewater flow could be reduced to 250 gpm by minor changes. As shown, inplant modifications which allowed installation of a 40 gpm rather than a 250 gpm end-of-pipe treatment facility saved $1.2 million. Actual savings was much greater, because premium costs for rapid construction of a 250 gpm wastewater treatment facility would have been much more than for the 40 gpm facility. (Premium costs are not included in Table 4, so that a direct comparison can be made with the venture guidance appraisals for the larger treatment facilities.)

Table 4. SAVINGS

DILUTE WASTE WATER TREATMENT		
250 gpm TREATMENT FACILITY		$7,300,000
40 gpm TREATMENT FACILITY		- $6,100,000
	SAVINGS	$1,200,000
RINSE WATER URANIUM REMOVAL		
22 gpm TREATMENT/CLARIFIER/FILTER		$2,500,000
6 gpm EVAPORATOR		- $1,100,000
	SAVINGS	$1,400,000
	TOTAL SAVINGS	**$2,600,000**
WASTE WATER REDUCTION		
RINSE WATER REDUCTION		$640,000
STACK SCRUBBER RECYCLE		$160,000
QUENCH WATER RECYCLE		+ $300,000
	COST	**$1,100,000**
	NET SAVINGS	**$1,500,000**

Installation of flow limiting orifices in rinsewater supply pipe to existing production lines had also demonstrated that dilute effluents containing uranium, that had to be removed by a separate pre-treatment facility, could be reduced to 22 gpm by minor changes. The flow reduction study recommended inplant plant modifications which allowed installation of a 6 gpm evaporation rather than a 22 gpm pre-treatment system with clarifier and filter. As shown, this too saved $1.4 million in construction costs. In addition, the evaporator was much easier to operate and more efficiently removed uranium. Steam limitations would have prevented installation of a larger evaporator.

As shown in Table 4, the total construction cost of the rinsewater reduction, quench water recycle and stack scrubber recycle system was $1.1 million dollars. (This does not include the cost of inplant modifications for wastewater transfers to treatment facilities that would have been needed even with no flow reduction.) The rinsewater flow reduction systems have proven reliable, needing little operator attention or maintenance other than replacement of conductivity probes. The quench water recycle system has proven equally reliable. Daily makeup of the filter aid mix tank, media roll replacement, and filter cake disposal have become part of routine solution control and material handling operator duties. Purchase of raw process chemicals has not noticeably changed, and the large reduction in process water useage did not appreciably lower operating costs because of its low cost. Hence, inplant modifications did not significantly change the internal operating costs of production buildings, and they greatly reduced the size of the wastewater treatment facilities.

Note that $7,000 in construction costs were saved for each gallon per minute of wastewater flow reduction, which is less than initially estimated. The venture guidance appraisal for the 250 gpm treatment facility was based on a continuous flow design. However, the flow reductions allowed construction of a 40 gpm batch operated facility that better matched M-Area needs. The size of a batch facility is larger than a continuous flow facility, so savings were less. In addition, construction costs do not decrease linearly with wastewater flow. As the size of a treatment facility decreases, its cost asymptomatically approaches a minimum cost. Hence, the cost savings for each successive flow reduction became less and less. This was considered during final assessment of recommended inplant modifications.

Benefits of Wastewater Flow Reduction

In addition to the large reduction in overall program costs, wastewater flow reductions were very important to achieving program goals. Treatment of more concentrated wastewater increased the pollutant removal efficiency of the process allowing a cleaner effluent stream. Most important the time required to design, construct and startup the treatment facilities was greatly reduced by the smaller size allowed by the flow reductions. It is improbable that larger facilities for unreduced flow could have been completed in the short time required to comply with the federal mandate and still maintain Savannah River Plant operations.

This success story demonstrates the benefits as well as the accuracy of methods used in the M-Area Effluent Characterization/Flow Reduction Study. Onsite field work was completed in four weeks and the final report was issued in six weeks.

WASTEWATER TREATMENT: OPTIMIZING AN EXISTING SYSTEM

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Harris Corporation
P. O. Box 37
Melbourne, Florida 32902

Harris Corporation-Government Systems Sector in Melbourne, Florida, is a producer of communications and information processing systems, and technologically advanced prototypes for government agencies and commercial customers. The industrial wastes generated by the sector are by-products of the processing of printed circuit boards, photographic prints and negatives, hybrid integrated circuits, and plated metal parts, all produced on a small job-lot basis. In 1979, the state of Florida established stringent water quality standards for the its receiving waters. Because Harris discharged its treated wastewater directly to surface water, it became apparent that improvements in the wastewater quality were in order. Engineering studies were initiated in 1980, and by November, 1982, a new treatment system utilizing state-of-the-art technology was in operation.

In the four years since Harris installed this 180,000 gpd system, numerous modifications to the treatment scheme and operating procedures have been implemented to ensure compliance with strict discharge limitations. Recent efforts have been devoted to fine-tuning plant operation and automating various administrative functions in an attempt to reduce operating costs approaching $300 K per year. And, in keeping with both of these objectives, it was necessary to implement a logical and environmentally sound method for accomplishing in-plant treatment of concentrated wastes. This paper describes the problem-solving methods employed to achieve these goals and details the results of those efforts.

System Description

The system was designed to treat a design flow of 125 gpm, consisting of wastewater contributed by ten separate and distinct operations. These operations contribute wastewater that varies considerably both in types of contaminants and in volumes of wastewater produced, resulting in a waste stream of great complexity (Table 1). The collection system consists of four parallel pipes which allow for waste segregation; these pipes discharge into their respective equalization sumps at the head of the treatment system. Wastewaters are segregated as follows: (1) acid/alkali (A/A) for corrosives and non-chelated metals, (2) cyanide (CN), (3) hexavalent chrome, and (4) printed circuit wastes (PCT).

Table 1.
Waste Stream Contributors

OPERATION	CONTAMINANTS	
Printed Circuit Board Fab	Copper Tin Gold Phosphate Acids	Lead Zinc Fluoride Chelates Alkalis
Deionized Water Plant	Acids	Alkalis
Plating Shop	Copper Cadmium Cyanide Acids	Zinc Nickel Ammonia Alkalis
Materials & Processes	Same as Plating Shop	
Graphics (Photo Lab)	Organics Silver	Phosphate Acids
Aluminum Etch	Acid	Aluminum
Hybrid Integrated Circuits	Copper Lead Fluoride Acids	Gold Chrome Phosphate Alkalis
Chem Lab (PC Boards)	Tin Gold Nickel Acids Chelates	Lead Copper Fluoride Alkalis
Electroforming Lab	Copper Nickel Acids	Zinc Cyanide Alkalis

Figure 1 depicts the treatment scheme in the form of a flow diagram. Cyanide-containing wastewaters are subjected to standard alkaline chlorination in two-step destruction of cyanide to carbon dioxide and nitrogen. Sodium hydroxide and sulfuric acid are used for pH adjustment, and oxidation is accomplished using chlorine gas. Hexavalent chrome is reduced to the trivalent state in a patented process which uses small pieces of scrap steel. A pretreatment pH of 2.0 to 2.2 is maintained and chromium is reduced according to the following equation:

$$Fe^{o} + Cr^{+6} \rightarrow Fe^{+3} + Cr^{+3}$$

Pretreated wastewater from both the CN and CR systems is returned to the A/A sump for heavy metal removal.

Preliminary treatment of the A/A waste stream consists of the addition of aluminum sulfate to act as a coagulant and to effect oil and grease removal, and calcium chloride primarily for removal of fluoride and phosphate ions. This is followed by a neutralization step in which the pH is adjusted to approximately 9.1 by addition of sodium hydroxide to precipitate heavy metal hydroxides. Flocculation follows, aided by addition of an anionic polymer. The flocculated mixture flows by gravity into a settling basin sized for a two-hour retention period.

The treatment scheme for PCT wastewater is similar to that for A/A wastes with the inclusion of a patented pretreatment step for metal complex destruction. The pH is lowered to 2.0 - 2.5, calcium chloride is metered into the stream, and the wastewater flows through a rotating drum containing scrap steel. The chelates are tied up at low pH, presumably by calcium ions, and an oxidation-reduction reaction occurs between the iron contained in the steel and the heavy metal ions, especially copper. Precipitation of heavy metal hydroxides, flocculation and clarification steps follow.

Clarified water from both settling basins flows into a small treatment tank to which insoluble starch xanthate (ISX) is added for removal of trace heavy metals. ISX effects instantaneous removal of metal cations in low concentrations and is used here as a final polishing step to help meet discharge limits in the ppb range for heavy metals. Because ISX is insoluble, its introduction must be followed by a filtration step. Wastewater from the ISX tank is pumped through a continuous-cleaning sand filter and then through a diatomaceous earth filter. This dual filtration system was designed to remove both ISX and residual metal hydroxide floc particles. Finally, the pH of the treated effluent is adjusted to within discharge limits through the addition of sulfuric acid. State regulatory officials required the addition of a degasifier as a final step prior to discharge, to serve as a precaution against the discharge of any volatile organic compounds (VOC's) inadvertently finding their way into the effluent from process areas.

Surface water (direct) discharge is by authority of a state industrial wastewater treatment plant operating permit and an EPA/NPDES permit. Effluent concentration limits are presented in Table 2.

Figure 1

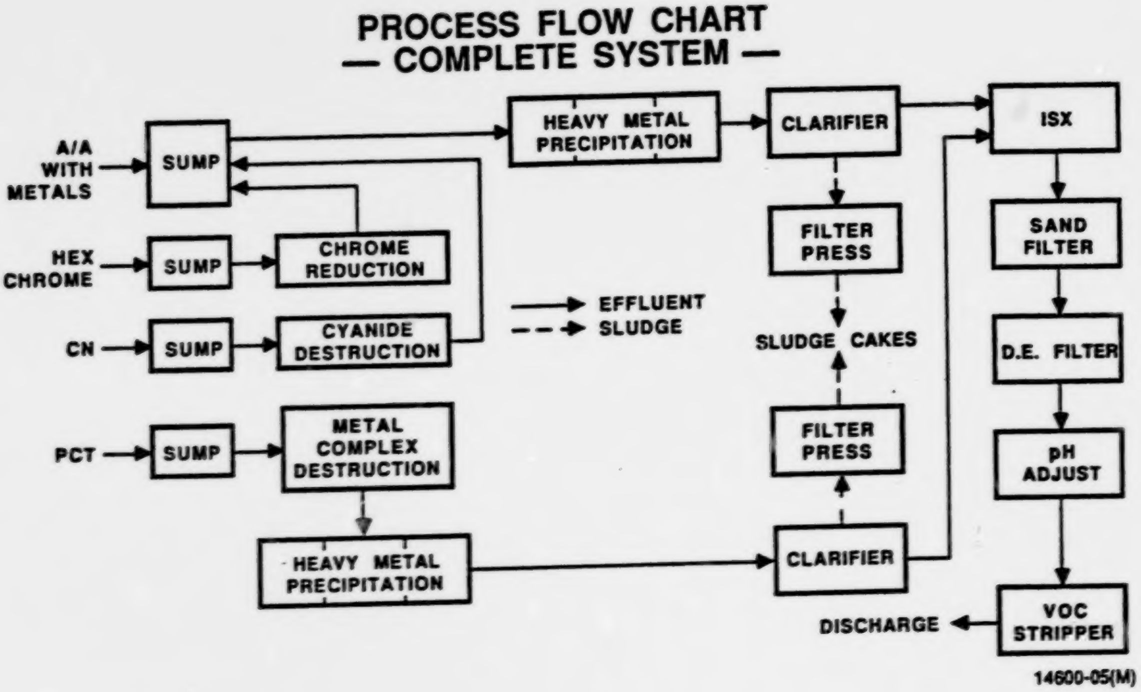

PROCESS FLOW CHART
— COMPLETE SYSTEM —
A/A WITH METALS
SUMP
HEX CHROME
SUMP
CHROME REDUCTION
CN
SUMP
CYANIDE DESTRUCTION
PCT
SUMP
METAL COMPLEX DESTRUCTION
HEAVY METAL PRECIPITATION
HEAVY METAL PRECIPITATION
EFFLUENT
SLUDGE
CLARIFIER
FILTER PRESS
SLUDGE CAKES
FILTER PRESS
CLARIFIER
ISX
SAND FILTER
D.E. FILTER
pH ADJUST
VOC STRIPPER
DISCHARGE
14600-05(M)

Table 2.
Applicable Discharge Limits

Monthly Average

Parameter	Permit Limit (ppm)
Cadmium	0.004
Chrome	0.05
Copper	0.08
Cyanide	0.005
Fluoride	10.0
Lead	0.03
Nickel	0.10
pH	6.5 - 8.0
Phosphorus	0.10
Silver	0.0002
TSS	10.0
Zinc	0.03

Improvements in Treatment Efficiency

1. A Sampling Plan. In the past, many difficulties had been encountered in "troubleshooting" permit violations. With so many varied operations contributing rinsewater to the waste stream, pinpointing a process problem becomes an almost insurmountable task, especially when flows are intermittent during the day and from day to day. In addition, with many discharge limits in the ppb range, analyses must be performed by a certified laboratory and the lab turnaround time often exceeds ten working days from the sampling date until notification of results. By the time results are reported, many problems are historical ones and investigative efforts are in vain.

Several steps have been taken and procedures modified to circumvent these inherent troubleshooting problems. Clean-outs were installed at the outfall of every operation for each collection pipe to which the operation is discharging, so that isolating samples can be taken when necessary. Each clean-out and manhole associated with the collection system was then given an alpha-numeric code name for ease in identification and to avoid communication errors. These names were painted directly on the sampling points and each point was located on a current site plan. Additionally, sampling points which could easily isolate treatment deficiencies were identified within the treatment plant itself. Now, when personnel were made aware of a persistent unacceptable concentration of any parameter, a sampling plan could be quickly and effectively designed by management and implemented by field or operating personnel. Finally, to aid in the isolation of "historical" problems, composite samples of all four sumps are drawn simultaneously with each treated effluent sample and these sump samples are properly stored pending notification of analytical results on the effluent. In this way, excessive concentrations (if they are not treatment-related) can at least be traced to one portion of the collection system.

In order to assess the long-term effectiveness of the treatment system and isolate target parameters for improvements, a three-year summary of effluent quality was compiled in the form of a permit violation "tally" (see Figure 2). The limit for copper concentration had been exceeded most often (nineteen times), followed by four other heavy metals averaging seven exceptions each over the three year period. There had been three violations of the TSS concentration limit. The concentration of no other parameter had violated its effluent limitation more than once in that time period.

2. Metals. Copper removal efficiency has steadily improved over the four years of plant operation, due to the ongoing efforts of plant personnel. In the first twelve months, effluent concentrations of copper varied widely and averaged 0.09 mg/l. The discharge limit for copper is 0.08 mg/l. Beginning in February, 1984, an investigation into the unacceptable copper removal efficiency was launched. Repeated rounds of samples were taken at key points in the treatment system and analyzed for copper. Results pointed to the A/A treatment system. Removal efficiency through A/A treatment averaged 86% resulting in a concentration of 0.20 mg/l in the A/A settling basin, while the PCT system was removing 99% of the incoming copper, treating to a level of 0.05 mg/l. The difference could not be attributed to incoming concentrations; the copper level in the PCT sump averaged almost five times higher than that in the A/A sump. Since the major difference between the two systems is the complex-destruction pretreatment step in the PCT scheme, personnel theorized that there must be a source of chelating agents discharging into the A/A sump. Characteristics of contributing flows were scrutinized.

The cause of the A/A treatment deficiency was found in a publication authored by Harris' supplier of photographic chemicals. Photographic developers and fixers typically contain a host of substances, including EDTA, thiosulfate, and sulfite, (along with a class referred to in the Bulletin as "sequestering agents") which will complex heavy metals. System design engineers had originally specified cyanide treatment for waste from the Graphics operation because

Figure 2

ANALYSIS OF PERMIT VIOLATIONS

1983-1985

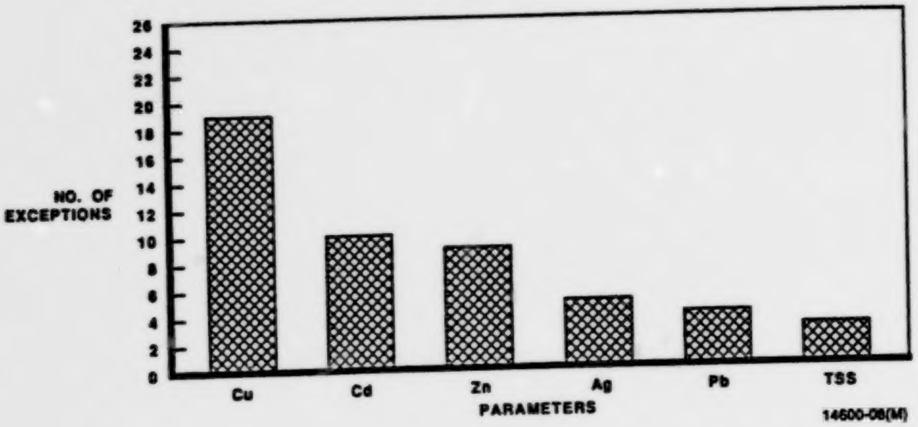
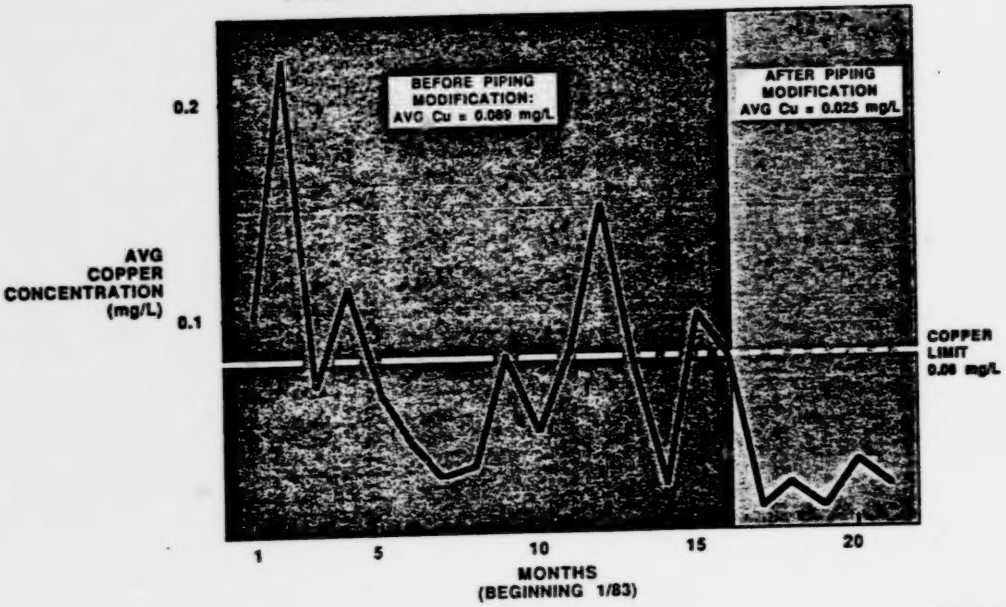


Figure 3

MONTHLY AVERAGE OF Cu CONCENTRATION FROM JAN/1983 TO OCT/1984



photographic solutions sometimes contained cyanide. The treated effluent from the CN system, of course, ultimately flowed back to the A/A sump and treatment system. The treatment scheme was subsequently modified to loop the pretreated CN effluent back to the PCT rather than A/A system. The result of this modification is depicted in Figure 3. Over the following four months, copper concentration averaged 0.02 mg/l.

Other steps which have been taken to avoid violations of the copper limit include (1) replacement of brass solenoid valves and metal fittings with teflon or stainless steel, particularly those associated with final polishing steps, to avoid leaching of copper (and zinc) into the effluent, and (2) implementation of daily testing of sump copper levels to enable prediction of treatment problems due to high copper loading from process areas.

Control of the concentrations of other metals of concern (cadmium, lead, zinc) was achieved primarily through the use of a jar test apparatus. Long used by engineers in the design of both municipal and industrial chemical treatment systems, this apparatus is also useful in the day-to-day operation of a system. Properly trained in its use, an operator can troubleshoot treatment and clarification problems "on-the-spot" and can, with the help of the analytical laboratory, optimize chemical and flocculent doses to achieve acceptable removal of metals and other inorganics.

3. Total Suspended Solids. Although not as persistent a problem as copper concentration, total suspended solids (TSS) levels occasionally exceeded permit limits. This condition was exceptionally frustrating to operators, considering the dual filtration system in place. Complicating the problem was the previously mentioned lag time between sampling and reporting of results. TSS levels were brought under control in two steps. First, a method had to be found whereby operators could monitor suspended solids in the final effluent. Turbidity and TSS are both measures of suspended matter in water; TSS is a direct measure of the weight of suspended solids in a given volume of water, while turbidity is an indirect measure of those same solids. The instrumental method of measuring turbidity involves measuring the intensity of light scattered by turbidity particles and calibrating against a standard. A turbidimeter was purchased and a series of final effluent samples were analyzed for both TSS and turbidity. The results were then graphed (Figure 4) and the correlation determined. A "line of best fit" was constructed and an operator's turbidity limit for the final effluent was established which would ensure compliance with permit standards.

Figure 4

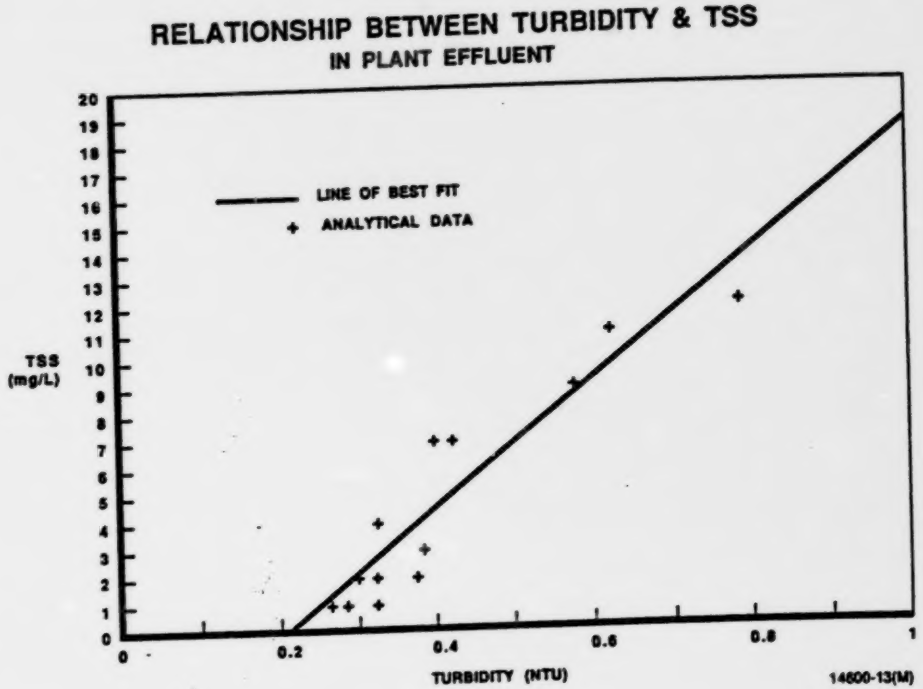
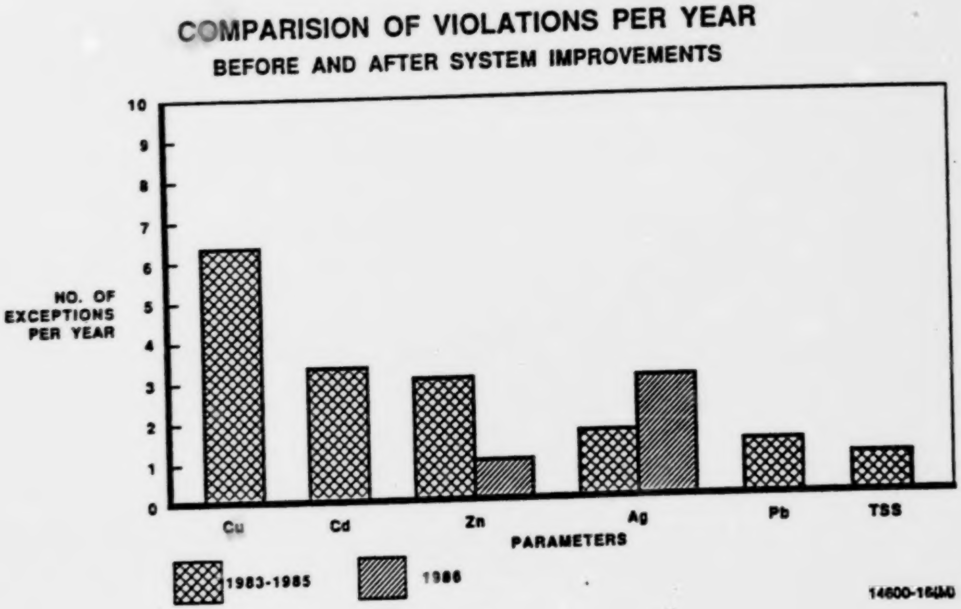


Figure 5



The second step in controlling TSS involved investigative work. Through turbidity measurements it was discovered that suspended solids often increased after the effluent was filtered. When this situation occurred, the solids were visible and resembled "snow", much like an aluminum floc. Samples of the effluent at various pH conditions were taken and analyzed for aluminum. Results are presented in Table 3.

Table 3.
Aluminum Concentrations
at pH 9.0 and 6.8

Aluminum (Form)	Before pH Adjust pH=9.0	After pH Adjust pH=6.8
Total	3.12 ppm	2.83 ppm
Dissolved	2.67	<0.05 ppm

This data demonstrated that the solids were indeed aluminum floc particles. When the pH of the effluent dipped to the 6.5 - 7.0 range from its previous range of 9.0 - 9.5, the solubility of the dissolved aluminum was exceeded and it began to precipitate out of solution. This situation was remedied by relocating the pH adjustment step to a point immediately prior to filtration. Other benefits were realized as a result of this modification to the treatment scheme. These will be discussed in a later section.

4. Results. Results of these measures taken to improve treatment efficiency are presented graphically in Figure 5. Permit exceptions were reduced from an average of 16.3 per year to 4 in 1986.

Cost Reduction

Data related to operational costs over the four years of plant operation was available in the form of monthly budget statements, monthly expenditures, purchase requisitions, and operator logs. However, in order to target areas for improvement, this data had to be compiled and summarized categorically. Table 4 presents operational costs by six-month period and by cost type. In order to compare costs over time without biasing the data with changes in flow volumes, flow-related costs have been annualized using the average daily flow for the entire 3.5 year study period. The final column presents average costs for each category for the

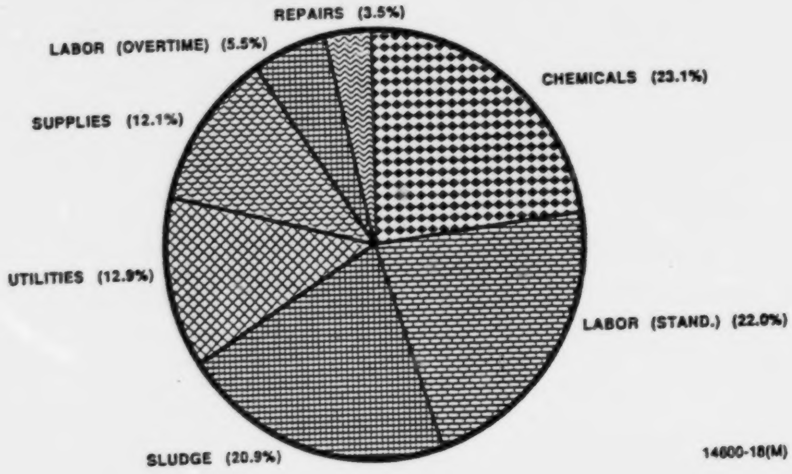
Table 4.
Plant Operational Costs
January 1983 - June 1986

ITEM	JAN-JUN 1983	JUL-DEC 1983	JAN-JUN 1984	JUL-DEC 1984	JAN-JUN 1985	JUL-DEC 1985	JAN-JUN 1986	AVERAGE
I. FLOW-RELATED COSTS ($/1000 GALLONS TREATED)								
CHEMICALS	3.53	3.28	4.19	4.54	2.98	3.32	3.45	3.58
SLUDGE DISPOSAL	3.56	3.15	3.45	3.62	2.72	2.66	3.91	3.29
UTILITIES (FLOW-REL.)	0.79	0.79	0.79	0.79	0.69	0.69	0.69	0.75
SUBTOTAL	7.88	7.22	8.43	8.95	6.39	6.67	8.05	7.56
ANNUALIZED (IN $K)*	123.4	113.1	132.0	140.2	100.1	104.5	126.2	118.4
II. NON-FLOW-RELATED COSTS (IN $K)								
PLANT SUPPLIES	4.4	13.6	16.3	29.7	16.7	8.8	13.2	14.7
REPAIRS	1.4	0.5	6.4	5.5	5.8	3.7	6.7	4.3
LABOR (STANDARD)	27.4	27.6	27.4	22.6	27.0	27.3	27.4	26.7
LABOR (O.T.)	0.3	7.6	7.2	11.5	7.6	9.2	3.7	6.7
UTILITIES (NON-FLOW-REL.)	11.0	10.4	10.0	9.5	9.3	8.9	9.0	9.7
SUBTOTAL (IN $K)	44.5	59.6	67.4	78.8	66.3	57.9	60.0	62.1
III. TOTAL ANNUALIZED COST (IN $K):	212.3	232.3	266.8	297.7	232.8	220.2	246.1	242.5

* USING AVERAGE ANNUAL FLOW OF 16 MG

Figure 6

PLANT OPERATIONAL COSTS



14800-18(M)

purpose of targeting improvement areas. Figure 6 presents this average cost data in the form of a pie chart. The three largest categories, comprising 66% of the total plant operational cost, are chemical supplies, standard labor costs, and sludge disposal, in that order.

The category labeled "Labor (Standard)" includes only the burdened wages of the two plant operators, with no overtime costs. For the purposes of our cost reduction effort, this cost category was considered uncontrollable. Therefore, efforts concentrated on costs in the other two categories, chemicals and sludge generation, along with an attempt to reduce flow to the treatment system.

1. Chemicals. In Figure 7, chemical costs are compared in dollars per thousand gallons treated. Using this data, four chemicals were targeted for extensive review based on their significant cost impact. A problem-solving matrix was constructed (Table 5) so that solutions could be "brainstormed". The first phase of the effort to reduce chemical costs was implemented in 1986, using the less costly and more easily implemented options identified in the matrix. Total cost savings projected to over $25,000 per year. The second phase, involving careful evaluation of the more difficult-to-implement options identified, is scheduled for 1987.

Although the matrix is discussed here more to illustrate a problem-solving technique than to detail individual cost-saving steps, one solution had significant impact and thus a discussion of this particular effort is worthwhile. In addition to being relatively costly to use, aluminum sulfate is commonly associated with the generation of a gelatinous, difficult-to-dewater sludge. Any reduction in aluminum use would probably bring two-fold benefits. The situation described in a previous section, in which pH adjustment was relocated to a point prior to filtration because of the precipitation of aluminum, pointed to the wisdom of recycling aluminum. The mechanism for recycling was already in place, with a continuous-cleaning sand filter poised to remove aluminum in the solid form and return it to the A/A sump, along with the reject wastewater (with solids) from the sand cleaning apparatus. All that remained was the development of a procedure for balancing aluminum concentration in the system so that it would neither continuously increase in the A/A treatment system nor drop low enough to reduce treatment effectiveness. This balance was achieved "in the field" by finding the optimum pH for aluminum precipitation, that level which would (based upon solubility curves) recycle the appropriate dose to the A/A system and bleed the remainder, in the dissolved form, out of the plant in the discharge.

Figure 7

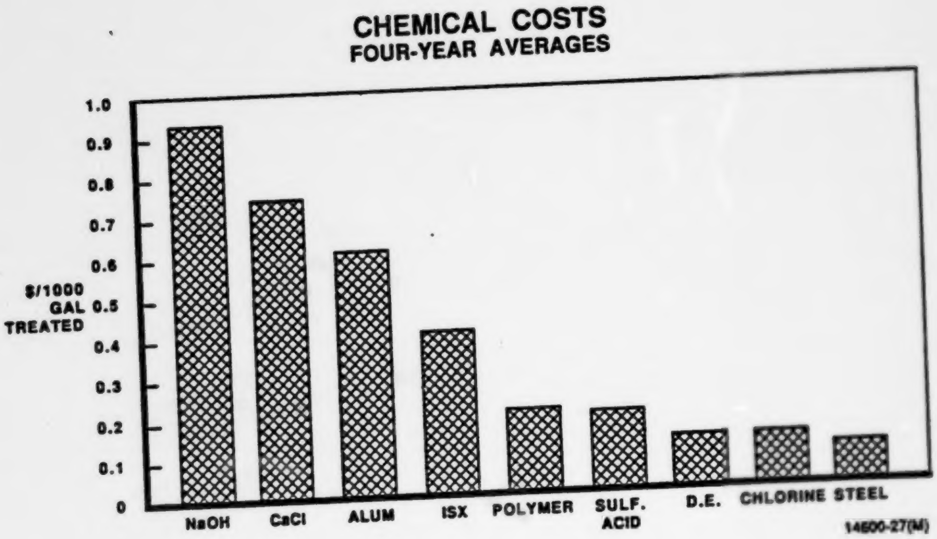


Table 5.
Chemical Use Analysis
Options for Cost Reduction

TARGET CHEMICAL	POINT OF USE	PURPOSE	OPTIONS	SELECT
Sodium Hydroxide	A/A and PCT-Neutralization/ Precipitation	pH Adjust	1.Reduce alum use in pretreatment	yes
			2.Evaluate alternative chemical (e.g. magnesium hydroxide	
			3.Increase pH in PCT pretreatment	yes
			4.Minimize "overshooting"	yes
			5.Precipitate metals at lower pH	
			6.Reduce flow through PCT system	
	CN Treatment	pH Adjust	1.Reduce flow through cyanide oxidation system	yes
Calcium Chloride	A/A and PCT Pretreatment	1.Removal of Fluoride and Phosphorus 2.Aid in Complex Destruction	1.Optimize dose	yes
			2.Evaluate alternative chemicals	
Aluminum Sulfate	A/A and PCT Pretreatment	1.Coagulant 2.Oil/Grease Removal 3.Fluoride Removal	1.Optimize dose	yes
			2.Evaluate alternative chemical	
			3.Recycle aluminum via sand filter	yes
Insoluble Starch Xanthate (ISX)	Final Polish at pH Adjust	Removal of trace heavy metals	1.Optimize dose	yes
			2.Evaluate effectiveness	
			3.Evaluate alternatives	

That measure alone, because it reduced aluminum sulfate use to only that amount necessary in the PCT system, resulted in an annual savings of almost $9000, not including savings in sludge disposal to be discussed below.

2. Sludge. The sludge generated is a typical metal hydroxide (F006) sludge, historically averaging 25-30% solids after dewatering in a filter press. Specific gravity is approximately 0.60. The average generation rate between 1983 and 1985 was 23 pounds per thousand gallons, or the equivalent of one twenty cubic yard container every three weeks. Disposal is in a secure landfill at a cost ranging from $133 per cubic yard in 1983 to $193 per cubic yard in 1986.

After implementation of the previously described aluminum-recycle procedure, the sludge generation rate dropped by 49%, from an average of 23 lbs per 1000 gallons to 11.7 lbs per 1000 gallons, and the solids content increased by approximately 45% to 40 percent. The total savings in sludge disposal attributable to the recycling of aluminum amounts to $26,400 per year. Figure 8 depicts the observed relationship between aluminum use and sludge generation. The exact mechanism by which sludge generation was reduced is unclear, since it was not the actual use of aluminum as a treatment chemical that was significantly reduced, but only the use of aluminum sulfate. It appears that the indirect effect on sludge generation and the percentage of sludge that is solids is related to the form in which the aluminum is introduced, i.e. recycled aluminum floc vs. aluminum sulfate.

One other cost reduction effort related to sludge generation is currently in the implementation stage. A metal hydroxide sludge dryer has been evaluated for use on the sludge generated by the Harris plant and has been found to be effective in reducing sludge volume by approximately 70%. This piece of equipment is scheduled to be installed in the first half of 1987 and projected cost saving is almost $20,000 annually. This will result in a payback period of two years, taking increased utility costs into account.

Operating costs were summarized using another format, presented in Table 6. Operational costs associated with each type of equipment or portion of the treatment system can be useful in targeting areas for improvement. In this case, it demonstrated that the cyanide treatment system is expensive to operate in terms of cost per 1000 gallons and contributors to that system should be evaluated carefully. It also indicated that, on an annual basis, the diatomaceous earth filter is expensive to operate and would be a good candidate for evaluation of alternative technology. This is planned in the near future.

Figure 8

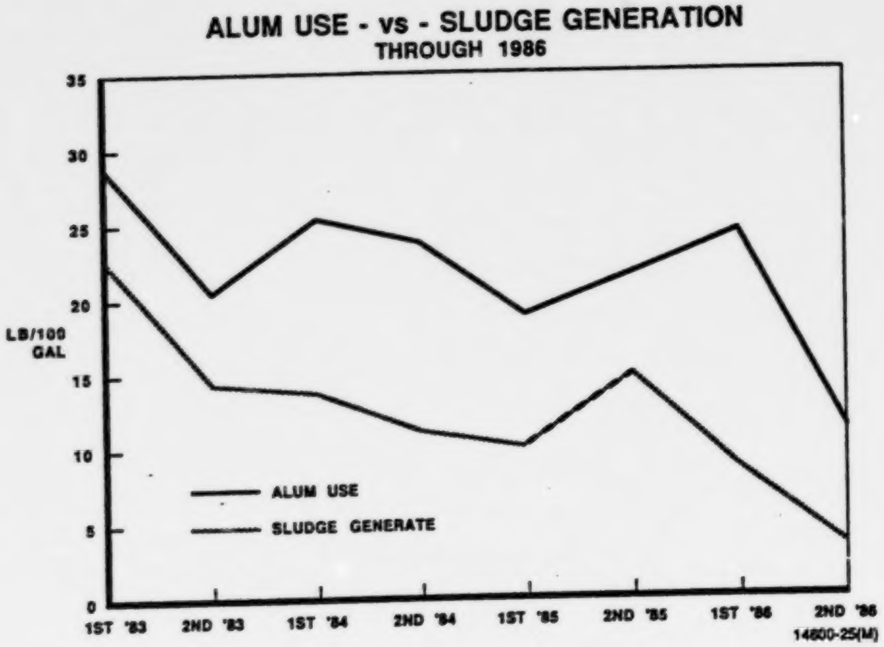


Table 6.
Equipment Operating Costs
Average Costs 1983 - 1986

$/1000 GAL TREATED

CATEGORY	PUMPS MIXERS	SAND FILTER	DIAT. EARTH FILTER	FILTER PRESSES	CONTROLS	COPPER REDUC. REACTOR	CYANIDE TREAT
SUPPLIES/ SPARE PARTS	0.14	0.08	0.47	0.25	0.25	0.66	0.33
REPAIRS/ SERVICE	0.08	0.01	0.16	0.01	0.08	0.26	0.21
CHEMICALS	0.00	0.00	0.17	0.00	0.09	0.47	1.62
LABOR	0.05	0.15	0.24	0.27	0.37	0.16	1.92
UTILITIES	0.96	0.07	0.07	0.13	0.20	0.24	0.26
TOTAL:	1.23	0.31	1.11	0.66	0.99	1.79	4.34
ANNUAL COST TO OPERATE (IN $ K)	19.3	4.9	17.4	10.4	15.5	13.6	12.4

Table 7.
Annual Cost Savings As a Result of Flow Reduction

SOURCE	ANNUAL SAVINGS
Unnecessary cooling water to A/A treatment: 1500 gpd	2300.00
Uncontrolled cooling water to A/A treatment: 2500 gpd	3900.00
Non-cyanide photographic waste to CN treatment: 10000 gpd	2800.00
TOTAL:	$9000.00

Table 8.
Results of Cost Reduction Efforts

BEFORE:	Annual Operating Costs		$242.5 K
	COST REDUCTION:		
	Sludge (alum reclamation)		- 26.4 K
	Sludge Dryer		- 19.1 K
	Chemicals		- 25.7 K
	Flow Reduction		- 9.0 K
AFTER:	Annual Operating Costs		$162.3 K
SAVINGS:		33% or	$ 88.2 K

3. Flow Reduction. Final efforts of this program to reduce operating costs centered on eliminating unnecessary flows through the treatment system, since flow-related costs amount to approximately $4.12 per thousand gallons (after adjusting for modifications and procedural changes described previously). Investigative efforts included weekend monitoring of flows at manholes and interviews with process personnel. Successful attempts are listed in Table 7, along with the associated annual savings ($9000 per year).

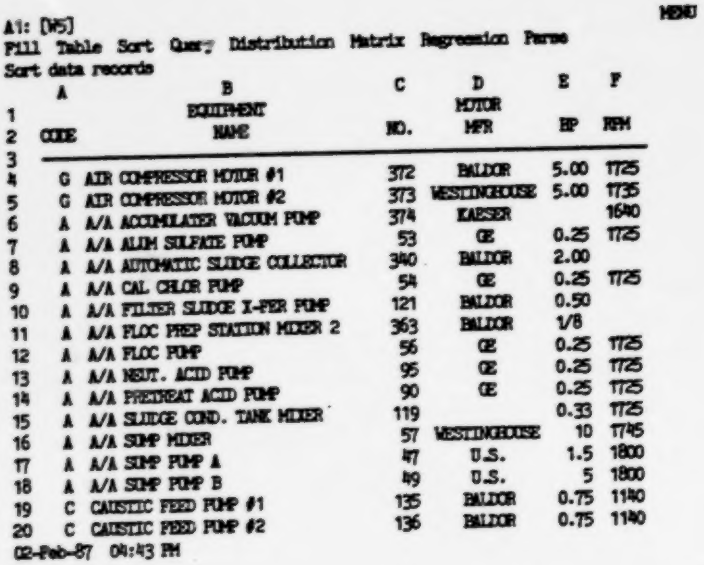
4. Results. A summary of the results of the cost reduction program is presented in Table 8. The total savings is $88,000 or 33% of the annual operating budget, with a potential for further reduction as a result of future actions, including evaluation of alternative chemicals and/or technology, and more extensive reductions in flow volume.

Automation

1. Objective. Soon after startup it became obvious that there would be a need for a modest information management system to track plant performance data, equipment inventory and preventive maintenance systems, agency reports, and plant expenditures. The system needed to be relatively inexpensive, easy to use and accessible to more than one individual. A microcomputer-based system seemed ideal for this situation, and an IBM PC-AT with 512 KB of RAM and a 20 MB hard disk was selected. This was coupled with an Epson FX-286 printer which could produce both draft and near-letter-quality style print and had the ability to graph data. Software applications would be many and varied, but relatively simple. The equipment inventory, for example, would require database capability but would consist of less than one hundred records. Several commercially-available software packages met these requirements; the combination selected included Lotus 1-2-3 for spreadsheet and database capability and Wordstar for word processing.

2. General Applications. The use of spreadsheet software for accounting and the production of reports is relatively straightforward and requires a minimum of training. Therefore, the first order of business was to develop simple spreadsheet templates for tracking of monthly expenditures and the required water quality report for the state environmental agency. Next, a Plant Operations Manual was compiled using the word processing software. This afforded the ability to continuously update operating procedures as new and more effective methods were developed.

Figure 9.
Section of Equipment Inventory Program
with Data Command Menu



```
A1: [W5]                                                          MENU
Fill  Table  Sort  Query  Distribution  Matrix  Regression  Parse
Sort data records
      A                  B                    C        D          E     F
1                    EQUIPMENT                       MOTOR
2   CODE               NAME                  NO.      MFR        HP   RPM
3   ---------------------------------------------------------------------
4      G  AIR COMPRESSOR MOTOR #1            372     BALDOR     5.00  1725
5      G  AIR COMPRESSOR MOTOR #2            373  WESTINGHOUSE  5.00  1735
6      A  A/A ACCUMULATER VACUUM PUMP        374     KAESER           1640
7      A  A/A ALUM SULFATE PUMP               53       GE       0.25  1725
8      A  A/A AUTOMATIC SLUDGE COLLECTOR     340     BALDOR     2.00
9      A  A/A CAL CHLOR PUMP                  54       GE       0.25  1725
10     A  A/A FILTER SLUDGE X-FER PUMP       121     BALDOR     0.50
11     A  A/A FLOC PREP STATION MIXER 2      363     BALDOR     1/8
12     A  A/A FLOC PUMP                       56       GE       0.25  1725
13     A  A/A NEUT. ACID PUMP                 95       GE       0.25  1725
14     A  A/A PRETREAT ACID PUMP              90       GE       0.25  1725
15     A  A/A SLUDGE COND. TANK MIXER        119                0.33  1725
16     A  A/A SUMP MIXER                      57  WESTINGHOUSE    10  1745
17     A  A/A SUMP PUMP A                     47      U.S.       1.5  1800
18     A  A/A SUMP PUMP B                     49      U.S.         5  1800
19     C  CAUSTIC FEED PUMP #1               135     BALDOR     0.75  1140
20     C  CAUSTIC FEED PUMP #2               136     BALDOR     0.75  1140
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Developing an equipment inventory involved more finesse with the spreadsheet software, but proved infinitely simpler than using a full-fledged database program. Lotus 1-2-3 includes its own database capability referred to as "1-2-3 Data Commands". It allows the user to build a database containing up to 256 fields and 2000 records and then manipulate that data in various ways including sorting, finding, and extracting records. When coupled with "macros", the database becomes a fast and efficient method to store and extract pertinent plant information. A segment of Harris' waste treatment plant equipment inventory is depicted (as it appears on the computer screen) in Figure 9 ; the actual database is much larger. Basic equipment information is entered in this first segment (left side). To the right, opposite the appropriate piece of equipment, the operator enters information related to repairs and service, including date, purchase order number, vendor, and cost. Now, any person with a need to find specific information can use the Data Commands feature. Examples include (1) sorting alphabetically by equipment name or manufacturer, or numerically by equipment number or horsepower, (2) extracting by manufacturer or equipment code, and (3) extracting by code to calculate costs associated with each treatment module. Because the database is still associated with the software's spreadsheet capability, total repair costs can be kept current for each piece of equipment and extracted as needed.

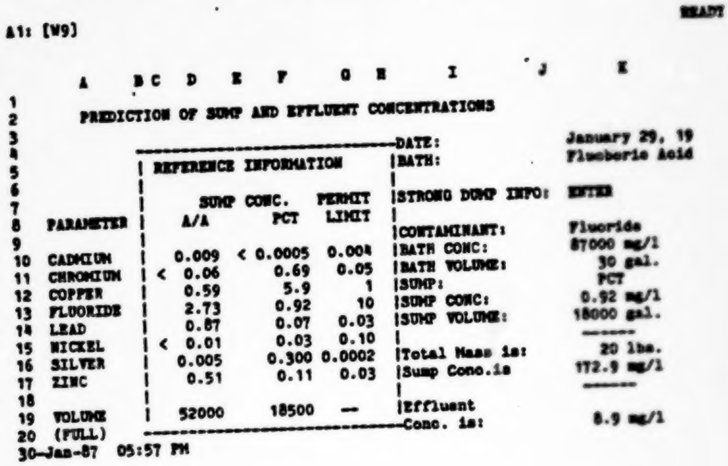
3. Treatment of Concentrated Wastes. In the past, because plant effluent limits were so stringent, only rinsewaters were piped to and treated by the industrial waste treatment plant. Concentrated baths from process areas were pumped into drums and shipped to a permitted treatment or disposal facility at great cost to Harris. However, as effective control of effluent quality became a reality, a safe and environmentally sound method for in-plant treatment of these solutions was required. The problem was two-fold. Operators had to understand the impact of each solution on overall treatment efficiency, and a means for scheduling the treatment of these baths had to be developed.

Both portions of the problem were attacked using the spreadsheet software as described above. Figure 10 depicts a strong "dump" model developed for use by operators which predicts the impact of any known solution on effluent quality, after treatment. The operator enters the information opposite the capitalized items on the right side of the screen, using reference information on the left side and available analytical data; the software calculates the last three values: Total Mass, Sump Concentration, and predicted Effluent Concentration. The user can then compare this predicted effluent quality with the permit limits listed in the Reference Information block and if the model predicts that the limit will be exceeded, can modify the proposed dump volume until the permit limit is safe.

Information derived from this model is then entered into the scheduling program, called QUEUE, so that a dump date can be scheduled. This program (depicted in Figure 11) uses the Lotus database. The operator enters data related to the solution itself, and the program predicts cumulative sump concentration, compares it to a stored limit, and schedules the dump on the next available date. These calculations are performed automatically by several macros stored with the program. Each day, the user can enter the program and use the Database Commands feature to extract all the dumps scheduled for that day; a printed copy becomes a permanent record.

Implementation of this program to handle concentrated process solutions in-plant has already resulted in a savings of $30,000 per year, primarily through the successful treatment of corrosive solutions containing copper and other inorganics.

Figure 10.
Model for
Prediction of Effluent Quality
As a Result of Treatment of Concentrated Wastes



```
                                                                      READY
A1: [W9]

          A      B C   D    E    F      G   H        I         J         K
1
2         PREDICTION OF SUMP AND EFFLUENT CONCENTRATIONS
3                                                                  January 29, 19
4                  ------------------------------DATE:             Fluoboric Acid
5                  | REFERENCE INFORMATION      |BATH:
6                  |                            |
7                  |     SUMP  CONC.    PERMIT  |STRONG DUMP INFO: ENTER
8      PARAMETER   |     A/A     PCT    LIMIT   |
9                  |                            |CONTAMINANT:       Fluoride
10     CADMIUM     |    0.009 < 0.0005   0.004  |BATH CONC:         87000 mg/l
11     CHROMIUM    | <  0.06      0.69   0.05   |BATH VOLUME:          30 gal.
12     COPPER      |    0.59       5.9      1   |SUMP:                 PCT
13     FLUORIDE    |    2.73      0.92     10   |SUMP CONC:          0.92 mg/l
14     LEAD        |    0.87      0.07   0.03   |SUMP VOLUME:       18000 gal.
15     NICKEL      | <  0.01      0.03   0.10   |                   ------
16     SILVER      |    0.005    0.300 0.0002   |Total Mass is:        20 lbs.
17     ZINC        |    0.51      0.11   0.03   |Sump Conc.is       172.9 mg/l
18                 |                            |                   ------
19     VOLUME      |    52000    18500    --    |Effluent
20     (FULL)      -----------------------------Conc. is:            8.9 mg/l
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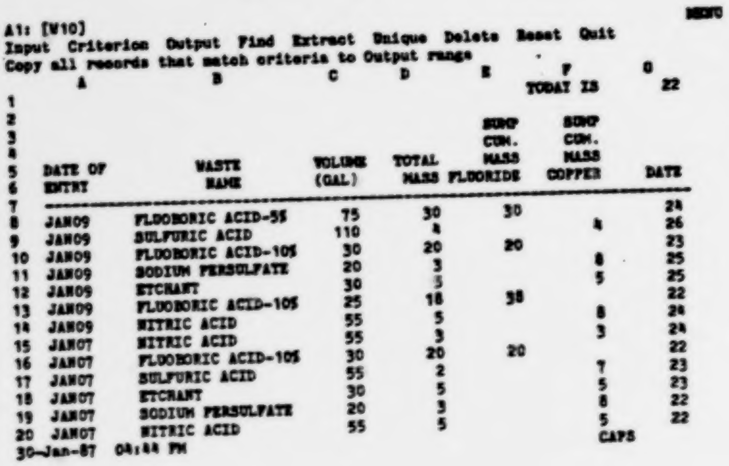
Figure 11.
QUEUE Program
for Scheduling of Concentrated Waste Treatment
with Data Query Menu



```
                                                                              MENU
A1: [W10]
Input  Criterion  Output  Find  Extract  Unique  Delete  Reset  Quit
Copy all records that match criteria to Output range
          A               B             C        D          E          F          G
                                                                   TODAY IS      22
1
2                                                         SUMP       SUMP
3                                                         CUM.       CUM.
4                                                         MASS       MASS
5   DATE OF            WASTE          VOLUME    TOTAL     MASS       MASS
6   ENTRY               NAME           (GAL)     MASS FLUORIDE     COPPER        DATE
7   ------------------------------------------------------------------------------ 24
8   JAN09      FLUOBORIC ACID-5%        75        30        30                   26
9   JAN09      SULFURIC ACID           110         4                    4        23
10  JAN09      FLUOBORIC ACID-10%       30        20        20                   25
11  JAN09      SODIUM PERSULFATE        20         3                    8        25
12  JAN09      ETCHANT                  30         5                    5        22
13  JAN09      FLUOBORIC ACID-10%       25        18        38                   24
14  JAN09      NITRIC ACID              55         5                    8        24
15  JAN07      NITRIC ACID              55         3                    3        22
16  JAN07      FLUOBORIC ACID-10%       30        20        20                   23
17  JAN07      SULFURIC ACID            55         2                    7        23
18  JAN07      ETCHANT                  30         5                    5        22
19  JAN07      SODIUM PERSULFATE        20         3                    8        22
20  JAN07      NITRIC ACID              55         5                    5
30-Jan-87  04:44 PM                                                  CAPS
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Summary

A logical and methodical approach to plant problem-solving exercises and cost-reduction can be of tremendous benefit to plant personnel in any endeavor to optimize an existing wastewater treatment plant. The causes of treatment problems must be efficiently isolated using an established sampling plan and analytical procedures, and operators must have appropriate monitoring parameters available to them to ensure that wastewater quality continuously meets applicable limits. Manipulation of available plant operating data will highlight less obvious solutions. Inexpensive and readily available software can automate many basic plant functions, saving operator time, producing much more consistent results in effluent quality, and providing a simple tracking mechanism for everything from operating costs to spare parts and equipment inventory.

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ELECTROLYTIC RECOVERY
THEORY, APPLICATION, ADVANTAGES

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Baker Brothers/Systems
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INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976 was enacted to protect the environment and to conserve our material and energy resources. Since 1980, the Environmental Protection Agency (EPA) has issued numerous final regulations implementing these congressional mandates. Today, without exception, all surface finishers are legally and morally obligated to comply with the pretreatment criteria set forth by these regulatory agencies.

In the past decade, conventional heavy metal precipitation technology has predominated the treatment methodologies employed. In general, this technique has met the required discharge limits. However, the problems associated with the disposal of solid residues (sludge) resulting from this treatment process are well documented as being unacceptable from the human health and economical points of view. Recognizing that perpetual containment of all dumped waste materials cannot be guaranteed, the Hazardous and Solid Waste Amendments (HSWA) were enacted in 1984. These amendments detail bans and restrictions on land disposal of hazardous wastes, and set forth a program of evaluation by the EPA to assess the impact of landfilling the listed hazardous wastes. If the EPA fails to make their final decisions within the scheduled deadlines, such wastes would be prohibited from land disposal unless the EPA grants a case-to-case petition. As a result, HSWA has further imposed substantial new responsibilities on all metal finishing facilities with regards to the recovery of waste metals and the minimization of sludge generation.

As a consequence of this federal direction, the associated costs of sludge generation, and the unpredictable price of possible future liabilities, waste generators are exploring the technologies and feasibilities of in-plant recovery and reuse. The most popular techniques currently being explored are: electrolysis, electrodialysis, ion exchange, evaporation, solvent extraction, and reverse osmosis.

Electrolytic techniques utilize electrical energy to cause the reduction of ionic metal species into the elemental, metallic state.

Electrodialysis is electrically driven ion exchange involving the concentrating of ionic metal salts by electrically forced migration across an ion exchange membrane.

Ion exchange relies on the surface affinities of synthetic resins and the difference in concentration gradients of the metal ions and exchanging ions.

Evaporation involves the control of heat and vapor pressures to concentrate dilute solutions by removing the excess water into the atmosphere.

Solvent extraction is a form of liquid ion exchange employing the density differences of two dissimilar liquids for the removal and concentration of the metal ions.

Reverse osmosis utilizes pressure to drive dilute, ionic metal species across an ion exchange membrane against the concentration gradient, into a concentrating compartment.

All of these techniques have their particular strengths and weaknesses but it is often electrolytic technology which is found to be the most desirable. This is because it is a familiar technology which utilizes the basic principles of electroplating. There is absolutely no sludge produced. Instead, the process results in metallic scrap which can be sold or reused. Electrolysis is also a cost competitive technique combining low capital equipment expense with a low operating cost.

Other benefits are particularly evidenced when comparing the more advanced principles of high-mass transfer electrolysis.

Basic Theory

The Electrochemical Cell:

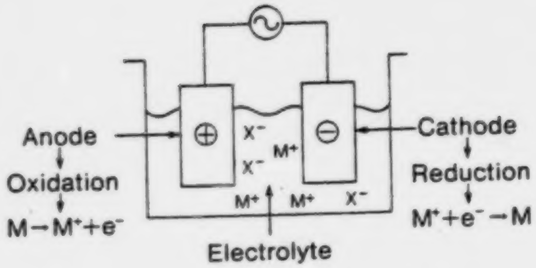

Figure 1. Electrochemical cell.

Electrolytic technology is an application of the science of electrochemistry, which is the study of processes and factors affecting charge transport at the interphase of an electronic and an ionic conductor. An electrochemical reaction is a chemical transformation involving a net electron transfer, i.e.:

$$2H^+ + 2e^- \rightarrow H_2$$

This heterogeneous reaction occurs at the interface between an electrode, which is the electronic conductor, and the electrolyte, which is the ionic conductor. When two electrodes are immersed into an electrolyte such that one electrode acts as an electron source and the other acts as an electron sink, with an electrolyte as the electron pathway, an electrochemical cell is defined.

The overall chemical reaction taking place in a cell is made up of two independent half-reactions, which describe the real chemical changes occurring at the two electrodes. The basic reactions occurring at these electrodes are oxidations and reductions. The cathode is the electrode that acts as the electron source and is the site of electrochemical reduction. Reduction, therefore refers to the gain of electrons. By driving the cathode to a more negative potential, the energy of the electrons is raised and they will eventually reach a level high enough to occupy vacant orbital states on certain ionic species in the electrolyte. The flow of electrons from the cathode to the solution is a reduction current.

The anode is the electrode that acts as the electron sink and is the site of the electrochemical oxidation. Oxidation, therefore refers to the loss of electrons. The energy of the electrons on the anode is lowered by imposing a more positive potential and, at some point, electrons on species in the electrolyte will find a more favorable energy on the anode and will transfer there. The flow of electrons from the solution to the anode is an oxidation current.

There are two general categories of electrochemical cells: galvanic cells and electrolytic cells. A galvanic cell is one in which reactions occur spontaneously at the electrodes when they are connected externally by a conductor. Galvanic cells are often employed in converting chemical energy into electrical energy, such as the battery in your car. An electrolytic cell is one in which reactions are made to occur by imposing an external voltage greater than the equilibrium potential of the cell.

Potential and Current:

The equilibrium potential of a cell is defined, for any given set of conditions, as that potential which results when electrons are crossing the electrode - electrolyte interfaces at the same rate in both directions. When the voltage applied by the external power source is equal to or less than the equilibrium cell potential, there is no flow of external current. As soon as the equilibrium cell potential is exceeded, current flows and chemical reactions occur. Overpotential is defined as that potential above the equilibrium cell potential.

Electrolysis refers to the chemical changes occurring at the expense of the applied electrical current. Electrowinning is the specific application of electrolysis for the extraction of metals from solution.

Each chemical substance has a unique potential difference based upon its molecular structure, its ability or potential to gain or lose electrons. As established by Tafel in 1905, the rates of electrochemical cell reactions are a function of the potential difference. The electrochemical reaction rate is the rate at which the power source pushes out and receives back electrons through the electrochemical cell.

In 1891, Nernst made the brilliant thermodynamic analysis that the electrical energy gained or lost when an electric charge is passed through an electrochemical cell is equal to the sum of the potential differences multiplied by the charge transferred in the reactions. He further observed that this sum is equal to the change in free energy which occurs in the net chemical reaction that takes place in the electrochemical cell. Thus, the electrochemical processes that occur at the electrodes in electrolysis depend, first of all, on the relative values of the electrode potentials for any particular electrochemical cell. Of several possible chemical transformations, the one associated with the minimum expenditure of energy will be carried out.

The critical potentials at which these processes occur are related to the standard potentials of the specific chemical substances in the system. A table of standard potentials, also called the electromotive series, is a direct result of the intense research provoked by Nersnt's thermodynamic analysis.

Those chemical substances with the highest potential to gain electrons, such as gold or copper, are the easiest to be reduced. Those substances with the lowest affinity for electrons, such as zinc or cadmium, are difficult to reduce, but easily oxidized with the metal losing electrons and entering the ionic state. The potential at which the reduction of hydrogen ions into hydrogen gas occurs is assigned the value of 0.000 volts as the standard comparison potential.

The table of standard potentials allows for the prediction of the preferred electrochemical reactions. These predictions are based upon thermodynamic considerations, and slow kinetics or catalytic effects might prevent a reaction from occurring at a significant rate in a potential region where the standard potential would suggest that the reaction was possible.

In 1834, Faraday proposed laws governing the quantity of a chemical substance consumed or produced at an electrode - electrolyte interface. Faraday observed that the quantity of substances being consumed or produced by an electrode reaction is proportional to the quantity of electricity consumed in electrolysis. Therefore, at 100% current efficiency, the mass of a substance consumed or produced is equal to the molecular weight of the substance divided by the necessary charge transfer, multiplied by the number of coulombs of charge transferred per period of time:

$$\text{Mass} = \frac{\text{Molecular Weight}}{\text{Charge Transfer} \times \text{Faraday}} \times \text{Current} \times \text{Time}$$

A Faraday is equal to 96,500 coulombs and is the amount of electricity required to bring about the oxidation or the reduction of one equivalent weight of any chemical species.

For the reduction of divalent copper ions, a current of one amp supplied for a time period of one hour will cause 1.184 grams of metallic copper to be produced at 100% current efficiency. This term is known as the electrochemical equivalent and is commonly expressed in grams per amp-hour.

Current is the rate of charge transport (the rate of electron flow) and is commonly expressed in amperes. One ampere, or amp, is equal to one coulomb of charge transferred per second. The potential, or the electrical pressure, required to cause a flow of one coulomb per second (one amp) is called a volt. Voltage is the driving force that struggles to overcome the resistance to current flow.

Mass Transfer:

When current density, the current applied per unit area, is studied as a function of electrode potential, there is a point reached at which the driving force of potential no longer increases the rate of charge transport. This is known as the limiting current. The rate of mass transfer of the ionic species from the electrolyte to the electrode surface

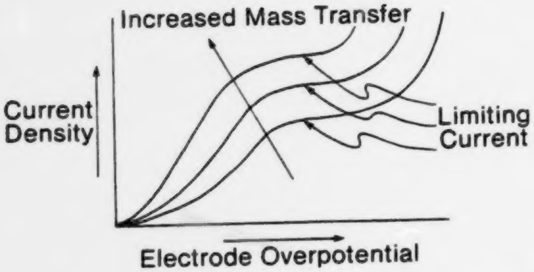

Figure 2. Limiting current curves.

dictates the limiting current. By increasing the rate of mass transfer, a higher limiting current is obtained through an increase in current efficiency.

The rate of mass transfer of the ionic species from the electrolyte to the electrode surface is dependent upon the ability of the ions in the bulk solution to transport through a diffuse layer and then the Helmholtz double layer. The diffuse layer is dictated by the kinetics of the reaction and results from the inability of the ions to transport from the bulk solution to the electrode as quickly as those ions at the electrode are being reacted. The Helmholtz double layer results from the adsorption of ions onto the electrode surface and then the adsorption of oppositely charged ions onto those previously adsorbed ions. The Helmholtz double layer, also called the electric double layer, exerts a major influence over the kinetics of charge transport. The physical chemistry of the Helmholtz double layer is dependent upon the electrode material, surface area, geometry, and surface condition, as well as the ions in the electrolyte solution.

The mass transfer kinetics are quantified by three variables: diffusion, migration, and convection.

Ionic diffusion is dependent upon the concentration gradient that develops between the electrode surface and the bulk solution. As ionic substances are being consumed at the electrode, the ions in the bulk solution attempt to reach equilibrium by movement into the depleted regions. Therefore, higher ionic concentrations facilitate replacement of the reacted ions at the electrode surface and this supports mass transfer. Ionic migration is dependent upon the applied electric field with ions being attracted to and repelled from the electrode. Ionic convection is dependent upon the movement of the bulk solution via agitated flow. Higher agitations result in smaller diffuse layers and facilitate mass transfer.

In solutions of higher concentrations, the effects of the concentration gradient are often sufficient enough to maintain a current efficient reaction. As the solution becomes more dilute, increasing the convection increases the mass transfer and improves the current efficiency. Ionic migration is facilitated by increasing the surface area. Increased surface area increases the electrode - bulk solution contact, thus minimizing the diffuse layer and increasing mass transfer.

When designing a commercial electrochemical cell, there are five categories of variables which must be considered: the solution, electrodes, mass transfer, electrical variables, and external variables.

The solution matrix and the desired electrochemical results dictate the materials of construction and specific orientations. When choosing or designing electrodes, the material of construction, surface area and surface geometry must all be considered. The modes of mass transfer are considered and optimized. The electrical variables of current and potential are determined based upon the quantity of electricity that is necessary per period of time. The effects and utilization of external variables such as temperature and pressure are also considered.

The engineering optimization of these five variables assures efficient, cost-effective performance from an electrolytic recovery cell.

Application

Recovery - Classical Vs. High-Rate Electrowinning:

Conventional electrolytic techniques utilizing parallel flat-plate electrodes are found to be very effective for the removal of recoverable metals from concentrated solutions. For solutions containing a few thousand parts per million (ppm) of metal, generally 90% current efficiency or higher can easily be achieved. However, for metals at concentrations of less than a few hundred ppm, this technique becomes very impractical and uneconomical.

As the electrowinning process proceeds, the solution adjacent to the cathode becomes depleted in metal ions and forms polarized layers. To be plated out, the metal ions must diffuse into and migrate across these layers from the bulk of the solution. Since the dilute rinses contain relatively much less ionic species, the diffusion rate is much lower than the deposition rate. The diffusion layer, therefore, becomes thicker and more depleted of ions. As a result, most of the applied current consumed is used to decompose water to form hydrogen gas instead of reducing the metal ions. Previous studies indicate that to make the electrolytic technique a more feasible approach for trace metal recovery, promoting the total ionic flux to the cathode by increasing both the cathode surface area and the mass transfer rate is essential.

In recent years, the need for advanced electrochemical reactor designs to accomplish high rate electrolysis has led to the development of various processes. Reaction cells with turbulent flow configuration; ultrasonic agitation; spiral-wound electrodes; fluidized-bed and packed granular bed; rotating cylinders and flow-through, three dimensional electrodes have been suggested and tested in the field.

Among all these innovations, the three dimensional, flow-through type electrode made of carbon-fiber has gained popularity in today's market due to simplicity and reliability. As depicted in Figure 3, the carbon-fiber electrowinning cell is capable of removing metal (e.g. copper) from low concentration rinse solutions to less than a level of 1 ppm in a shorter period of time. At the same time, the cell is maintained at a steady high range of efficiency (90-95%) throughout the entire process.

Theoretically, those metal ions which can be electroplated from

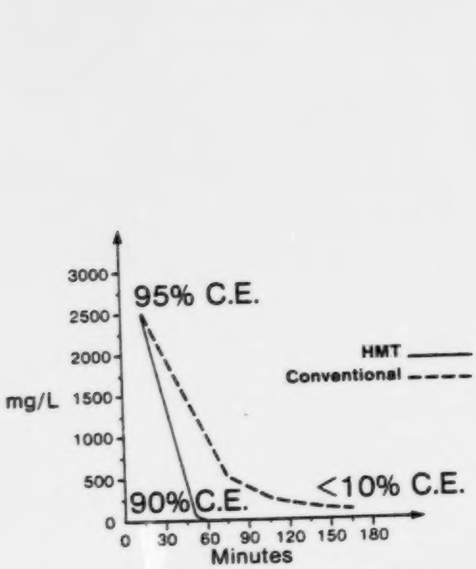

Figure 3. Efficiency of high-mass-transfer electrowinnning versus conventional electrowinning.

aqueous solution can be extracted by electrowinning. Therefore, common metals, such as copper, can easily be plated out while aluminum can hardly be removed. As pointed out earlier, each metal possesses its unique reduction potential. This special feature, coupled with the chemical behavior of its solution, will determine the practicality of recovering a specific metal by electrowinning. For instance, copper in an acid copper plating solution can typically be electrowon two to three times faster than extracting the same quantity of copper from a sulfuric-peroxide solution. Metals in various plating solutions, which can be economically recovered and feasibly removed to meet the pretreatment standards by the application of carbon fiber electrowinning are summarized in Figure 4 along with their respective recovery rates.

Carbon-Fiber Electrowinning:

The carbon-fiber electrode is a three dimensional flow-through type assembly, consisting of carbon fibers woven into layers of fabric secured to the electrical distribution feeder sheets in a plastic coated frame (See Figure 5). The primary characteristics of the carbon fiber is the extremely high surface-to-volume ratio which allows construction of an electrode with enormous active contact surfaces in a small volume to carry out the desired electrochemi-

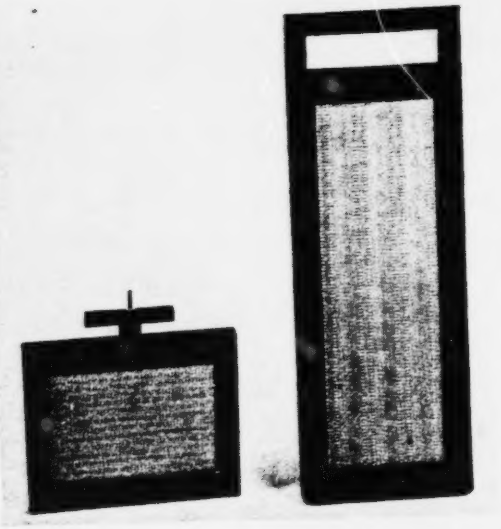

Figure 5. Carbon-fiber electrodes.

Metal	Solution	Recovery Rate
Cadmium	Cyanide	360 Grams/Hour/Meter^2
Copper	Electrolytic, Electroless, Etch	60-420
Gold	Acid, Cyanide	600
Tin/Lead	Fluoborate, Sulfate	85-270
Silver	Acid, Cyanide	600
Zinc	Cyanide	90-120

Figure 4. Practical applications.

cal reactions. In the electrodeposition process, these extended platable areas greatly minimize the diffusion layer and various polarization barriers of the mass transfer mechanism. Thus, the reactants can penetrate across the solid-liquid interfacial region with less resistance and be reduced at the cathode surface. The mass transfer flux is also greatly promoted by the tortuous flow pattern of the solution in the carbon-fiber electrode bed.

The carbon fibers are commercially produced by heating high modulus organic precursors, such as polyacrylonitrile (PAN), under controlled rates of temperature rise. Because of its active electrocatalytic effect on most metallic ions and relatively high hydrogen overpotential characteristics, the carbon fiber electrode can be operated with high current efficiency (>90%) at very low metal concentrations before the competing hydrogen reaction becomes predominant. This leads to low power consumption and less operating cost for treating the pollutants.

The carbon-fiber has been proven to be a technogically efficient and economically viable material for reduction of metal ions. Some of the other unique properties of carbon-fibers include:

- Chemically inert to most acids, bases and solvents
- Good electrical and thermal conductivity
- Excellent friction and wear characteristics
- Low density and relatively low cost per unit volume

Electrowinning in aqueous solutions inevitably requires employment of dimensionally stable anodes which retain their shapes and voltage characteristics even under the most aggressive electrochemical reaction conditions. In most electrolytes, the greater the ease of oxygen evolution reaction at the anode, the greater the likelihood that the anode will be insoluble. The type of materials useful as insoluble anodes in the electrowinning process is rather limited. Until the 1960's, graphite and lead were two of the few preferred anode materials. However, their high over potential requirement and degradable nature were one of the drawbacks that needed to be resolved at that time in order to derive a more efficient and low operating cost electrolytic cell.

The selection of the anode materials of construction depends to the greatest extent on the reaction requirements and the electrolytic condition under which they operate. Ever since titanium has become commercially available in large quantities, important break throughs have been made with respect to the development of the electroactive anode coatings. Recent advances in the technique of solid phase roll bonding have resulted in anode structures of titanium, niobium and tantalum with continuous coatings of precious metals, metallic oxides and/or their alloys. As is required, this new generation of anodes satisfies the criteria of an active surface and a stable coating on an inert, highly conductive substrate. To optimize the electrowinning performance, in conjunction with the carbon-fiber electrode, dimensionally stable anodes with metallic bonded coatings such as plantinum, iridium,

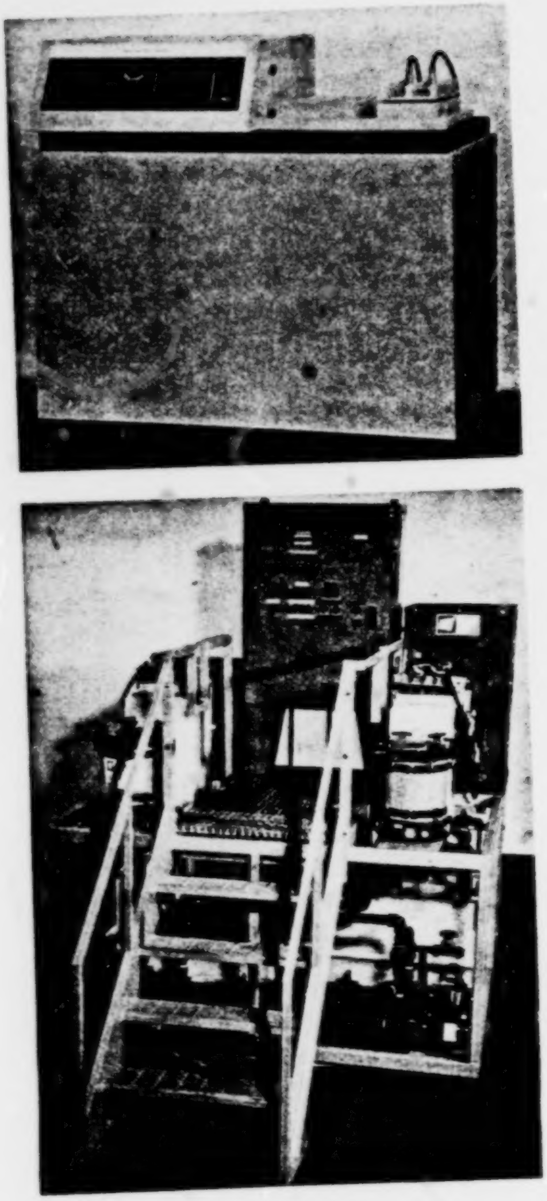

Figure 6. (Top and bottom). Two commercially available HMT electrowinning systems. The bottom system has a recovery capacity 10 times that of the top unit.

ruthenium and their oxides, as well as fluoride-resistant metal composites, have been incorporated into the advanced cell design for the pollution control application.

As compared to the conventional anode, the advantages of dimensional stability of the recently developed metal coated anodes are illustrated in the following:

- Produce high purity product with low bath contamination

- Low oxygen overpotential reduces cell power cost.

- Corrosion resistance provides high durability and stability.

- Substantially lower operating and maintenance cost.

The High-Mass-Transfer (HMT) electrolytic recovery system (See Figure 6) equipped with the above described carbon-fiber and dimensionally stable electrodes, is specifically designed to capture low concentration of plating metals in waste solutions. The process is comprised of two basic electrochemical steps: metal electrowinning and electrorefining.

The dilute, metal laden solution which functions as the electrolyte in the electrowinning cell, is pumped and recirculated through the porous carbon-fiber cathode assemblies in a closed-loop flow circuit. As the metal deposition progresses, the cathodes will maintain their steady removal efficiency until the majority of micropores, which contribute most of the surface area in the carbon-fibers, are occupied by the plated metal. At this point, the loaded cathodes are transferred to the electrorefining cell where they will be regenerated by anodic stripping of the accumulated metal. During the refining process, the dissolved metal ions migrate through a permanent electrolyte in the cell and deposit onto stainless steel starter sheets from which they are peeled off as non-toxic, resalable product. These two processes are controlled independently and function simultaneously to achieve minimal operation time.

For the best results, the waste solution to be treated should contain only one kind of metal. The system can be set up to operate in a batch recovery mode, by which the system functions as a treatment device primarily. All dragout bath dumps containing the same metal ion (e.g. copper) will be combined in one tank and recirculated through the electrowinning cell. The metal in the solution is removed to the acceptable discharge concentration prior to disposal of the treated batch. The system can also serve the function of continuous recovery. In this mode, the metal is continuously reclaimed by the electrowinning cell while the dragout tank is kept at a constant low concentration level (say 100-200 ppm). The subsequent running rinses are normally sufficiently dilute to be discharged.

Economics of Metal Recovery

Whenever pollution abatement or recovery technologies are discussed, the cost to install and operate a system is just as important a consideration as the technological capabilities of the system. The capital investment cost for a treatment system principally depends on two factors: geographic location of the plant and characteristics (both quantitative and qualitative) of the wastes generated. These two factors when combined together will determine the complexity and the physical size of a system. To obtain an accurate capital equipment cost, each system must be analyzed on an individual basis.

After a system is defined, the operating cost can be evaluated based upon: a) the sludge disposal cost, b) the treatment chemical cost, c) the utility cost and d) the labor cost. A comparison of these variables is illustrated in Figure 7, for running a typical precipitation/clarification system and a carbon fiber electrowinning

Chemical Precipitation (One 55 Gal. Drum Sludge)		**HMT Electrowinning (Dragout Recovery)**
$4	Neutralization (NaOH)	$4
$29.5	Precipitation (NaOH, $FeSO_4$)	None
$4.5	Flocculation (Polyelectrolyte)	None
$30	Sludge Drum	None
$135	Sludge Disposal	None
Yes	Electric Power	$13
Yes	Other Utilities (Water, Air, Etc.)	None
$120	Labor	$48
Forever	Liability	None
None	Salvage Copper Value	$-12

$323 – Minimum Total Cost – $53
$9.2 – Minimum Cost/Pound Metal – $1.5

$270 Savings/Drum
259 Days Payback

Figure 7. Cost comparison for removal of 35 lbs. of copper.

cell. Rather than attempting to derive a specific comparison with precise figures, Figure 7 intends to bring out the relative magnitude of the different costs involved in the operation of these two approaches. It is noticeable that sludge disposal and chemical usage account for about 60% of the total operating expenditures. These two economic factors obviously offer the best opportunity for cost savings.

As stated before, electrowinning is the extraction of metals from solution under the influence of an applied current. No treatment chemicals are necessary to carry out this process. The only consumable required is electricity. To produce one pound of metal it normally takes 3 to 4 KWH of electrical power. In most cases, the electricity cost is offset by the value of the recovered metal. In addition to the benefits of low operational cost and a positive return on investment, the system generates no sludge and, therefore, eliminates the permanent liability of sludge disposal. It is self-evident that the labor cost is also considerably reduced to a great extent by deleting the necessity of sludge and chemical handlings. All these substantial savings, tangible and intangible, lead to a very attractive pay back period even for the recovery of those less expensive metals.

The carbon fiber electrowinning technique has successfully demonstrated a new perspective for today's pollution control philosophy. That is, to achieve the goal of full regulatory compliance by recovery and conservation of our precious resources.

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WASTE TREATMENT AND RECYCLING OF MIXED WASTEWATER FROM A METAL FINISHING COMPANY

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Background

An electroplating shop in Providence, Rhode Island accepted a challenge to install a waste treatment system to remove pollutants from the rinse waters in their plating operations. The regulatory body, Narragansett Bay Commission (NBC), requires very stringent effluent standards effective in two tiers covering a time span of shorter than 18 months. The company, International Chromium Plating Company, does a variety of plating work including electroless nickel, bright nickel, chromium, acid copper, cadmium, zinc, and chromate conversion coating, etc. As a result, a variety of heavy metals and cyanides constitute the contaminants in the rinse water. International Chromium had over the previous two years installed triple rinse tanks, flow restrictors, and electrolytic reducing devices to remove metals. The company had been making conscientious and intelligent efforts in terms of in-process dragout recovery, avoiding spent bath dumps and spill controls. However, it became obvious that a custom-designed waste treatment system was needed.

Objective

The objective of the waste treatment project is to meet the discharge limitations required by the Narragansett Bay Commission. These limitations are listed in Table 1. The design of the treatment system should also take into consideration sludge minimization, and flexibility of operations and maintenance for in-house personnel.

Preliminary Engineering

Wastewater samples were taken and composited for four consecutive days in the last quarter of 1985. The results of these tests as indicated on Table 2 show that the average value of the four days testing of all components except lead exceeded the July 1, 1987 standards and that current standards were exceeded for cadmium, chromium, zinc, and total cyanide during some part of the testing period. It must be noted that the samples were taken in the flow from the combined waste stream of boiler discharge, non-contact cooling water and wastewater (rinses). The rinse waters have an average flow of about 1000-1200 gallons per hour. Sanitary waste will be discharged at the downstream of the proposed end-of-pipe wastewater treatment system. Steam condensate generated from the process heating continues to be discharged in a similar manner as sanitary waste. The cooling water used to cool the degreaser will either be pumped to a roof-top cooling tower to reduce the water temperature for recycling, or diverted for process rinse. These two water conservation schemes can be practiced interchangeably to accomodate the seasonal variation and to provide operating flexibility. The final process rinse water will be treated in an end-of-pipe treatment system (which is designed to meet compliance with the July 1, 1987 standards) prior to its discharge to the city sewer.

The usual method of treating metal-bearing wastewater using hydroxide precipitation was not expected to consistently achieve the stringent effluent standards required for the Narragansett Bay Commission. Therefore, an advanced treatment process had to be selected. Electrodialysis, reverse osmosis and ion exchange were among those considered.

Both electrodialysis and reverse osmosis have capabilities of producing high-quality water(1,2) suitable for recycling. However, ion exchange can be custom designed to remove specific groups of contaminants, thus rendering the effluent suitable for discharge (i.e., within discharge limitations). Both electrodialysis and reverse osmosis were not selected because of the potential disposal problem due to the generation of concentrated streams from either process. Thus, ion exchange was conceived as the work horse of the designed treatment system. The IX system was to consist of a simple cation resin bed followed by a pH adjustment system. The result would be the discharge of a neutralized salt-laden, but virtually metal- and cyanide-free effluent.

Design Detail

Initially, a cyanide treatment system to remove cyanide in the wastewater was considered as necessary prior to entering the ion exchange units. It was discovered that cyanides, along with other contaminants, could be adsorbed effectively in a three-bed system. This would considerably reduce the cost of the entire system. The cyanides along with other anions would then be removed simultaneously. This would shift the emphasis of the IX system toward producing an effluent with a low level of dissolved solids.

The selected IX system consists of the following:

(1) Cartridge filters

(2) Carbon adsorption bed

(3) Three-bed IX columns (consisting of strong acid cation, weak base anion and strong base anion resins)

(4) Precipitation hopper

(5) Heat exchanger (to heat up caustic regenerate)

(6) Acid regenerant waste tank

(7) Backwash tank

(8) Acid and caustic metering system

The exhausted IX columns are regenerated by hydrochloric acid and caustic soda for both the cation and anion resin beds respectively. The regenerant wastes are then collected in tanks and sequentially pumped to the precipitation hopper. The control instruments for the oxidation/reduction potential, and pH are used as indicators for completing cyanide destruction (oxidation by hypochlorite), chromium reduction (by sodium bisulfite) and metal precipitation(by hydroxide). The precipitate is allowed to settle using polymers to help coagulation, then the sludge thickened and drawn off to a sludge holding tank. The supernatant is a dischargeable effluent. The provision is made to use the IX effluent to dilute the supernatant which at times could have marginal discharge quality.

At the tail end of the treatment system a filter press was added to enable the plating shop to concentrate the metal hydroxide sludge and reduce the volume of hazardous waste for offsite disposal. A block flow diagram of the entire treatment system is shown in Figure 1.

The ion exchange resin configuration is arranged with the assistance of the selected vendor(3) as follows:

(1) Strong acid cation resin to adsorb cationic heavy metals, and break cadmium cyanide complexes and partially break copper cyanide complexes.

(2) Weak base anion resin to adsorb copper cyanide complexes, chromate and a good portion of the anions of the mineral acids such as sulfate, chloride, etc.

(3) Strong base resin to adsorb the residual free acids such as free cyanide, boric acid, and any residual anions of the mineral acids.

This effectively facilitates the ion exchange process and is the only end-of-pipe waste treatment system that is capable of handling mixed wastewater from various rinses. Separate pretreatment for cyanide destruction is no longer required. The dissolved solids loading onto the ion exchange columns are thus tremendously reduced due to the elimination of cyanide pre-treatment. This will enhance the service capability of the IX because the run length is increased as a result of less frequent regeneration.

Composition of the combined rinses was checked in sample testing which yielded the results shown in Table 3. The results show that there are approximately 5.2 milli-equivalents of anions per liter and 3 milli-equivalents of cations per liter of rinsewater. According to the vendor, these values are still within the limits which will yield successful performance.

Initial estimates of the ion exchange column sizes call for a 24-inch diameter containing about 15 cubic feet of the appropriate resin. For complete demineralization, these columns may be expected to treat about 22,000 gallons of rinses, or about 2 days worth of operation. During this time only about 3-6 pounds of mixed heavy metals would have been removed.

Discussion of Expected Performance

The rinse waters from metal finishing operations traditionally are treated in separate streams, i.e., through cyanide oxidation and chromium reduction, followed by chemical precipitation of heavy metals prior to discharge. Recently, the literature has indicated that substantial interest has been generated in treating the mixed waste stream by the ion exchange process, or in recovering metals by individual processes. Simultaneously the system would be producing an effluent suitable for discharge.(2) It was suggested however, that an IX system installed on the rinses following the main plating process would not allow the total effluent to meet the standards, and conversely, an IX system for total effluent would make metal salts recovery infeasible. On the other hand, the use of the IX system to capture contaminants at the end-of-pipe to produce acceptable effluent levels without considering recovering of metal salts by the same IX has not yet been ruled out. Needless to say, it would be economically attractive if the treated effluent can be recycled without extra expenses incurred from operations and maintenance.

Previously, another electroplating company was faced with a similar type of challenge.(4) Springfield Electroplating Company in Vermont had been discharging wastewater to the Black River until 1973. The effluent limits required by the State of Vermont called for 0.03, 0.50, 0.50, 1.0, and 0.3 mg/l respectively for cyanide, chromium, copper, nickel, and cadmium. It is obvious that the first three parameters are more stringent than NBC's July 1, 1987 standards, while the last two parameters are more lenient. The same system, and virtually the same size of IX equipment as was engineered for International Chromium Plating Company was installed for the Springfield Electroplating Company. The treatment results indicated that deionized water was produced and suitable for make-up and rinsing in the plating room. The only effluent discharge came from the batch-treated regenerant. The discharge was approximately 2,500 gallons every three weeks. The effluent met the standards.

Depending on the composition of the raw water used for process rinse, and the chemical concentrations of the final rinse water, the IX system can be a flexible tool to achieve the goals of water recycling and compliance with regard to discharge standards. It is more advantageous to reduce the pollutant loading in the process in order to prolong the service runs of the IX. The less frequent the IX columns need to be regenerated, the more time is available for the operator to spend on improving the process, and the longer time the sludges in the precipitation hopper can be allowed to settle to produce clear effluent. The regenerant waste can be treated in-house to reduce offsite treatment costs while also helping to contain/control the risks associated with the liability of hazardous waste. Otherwise, it can be handled by a central recovery plant at a slightly higher cost.

The ability to produce recyclable water for process rinse would go a long way toward extending the IX service mode because invariably some salts that are introduced from the city water will have been taken out of the recycled water. On the other hand, the longer the service runs, the greater the opportunity there is to allow build-up of certain salts in the recycled water. This would effect the rinses. Therefore the close-loop system must be purged occasionally and introduced with fresh make-up.

The strategies for successful employment of the IX system to achieve the goals include the following: constant improvement to reduce metal salts loading to the system by in-process recovery, waste minimization and water conservation; close monitoring of the system performance to prevent leaks; and flexibility of solids handling to free up the system for continuous operation.

The IX system that has been engineered on this project is an integral part of the plant operations. International Chromium Plating Company is currently installing the described waste treatment system and ancillary equipment with the anticipation to meet the July 1, 1987 effluent standards several months ahead of time.

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Table 1
Narragansett Bay Commission
Effluent Discharge Limitations

	Effective 6/30/84 For Electroplaters *				Effective 2/15/86		Effective 7/1/87
	Over 10,000 GPD		Under 10,000 GPD		for Metalfinishers*		for All Users
	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
Cadium	1.2	0.7	1.2	0.7	0.69	0.26	0.02
Chromium (Total)	7.0	4.0	-	-	2.77	1.71	1.11
Copper	4.5	2.7	-	-	3.38	2.07	1.13
Cyanide (Total)	1.9	1.0	5.0 (amena[illegible]	2.7	1.20	0.65	0.52
Lead	0.6	0.4	0.6	0.4	0.69	0.43	0.58
Mercury	-	-	-	-	-	-	ND
Nickel	4.1	2.6	-	-	3.98	2.38	0.32
Silver	1.2	0.7	-	-	0.43	0.24	0.072
Zinc	4.2	2.6	-	-	2.61	1.48	1.45
Total Toxic Organics	2.13	-	4.57	-	2.13	-	2.13
Total Metals	10.5	6.8	-	-	-	-	-
pH	5.0 - 10.0		5.0 - 10.0		5.0 - 10.0		5.0 - 10.0

All limits are in mg/l except pH which is standard units.
* As defined by Federal Regulations (see 40 CFR 413 and 433).
MAX shall mean maximum.
AVG shall mean average.
ND shall mean not detectable when analysis is done in accordance with EPA approved methods.

Table 2
Comparison of Effluent Chemical Concentrations With NBC's July 1, 1987 Standards

Chemical Name	NBC Stds Effective 7/1/87 day max. Conc. mg/1	4 Day Composite			
		10/28/85 mg/1	10/29/85 mg/1	10/30/85 mg/1	10/31/85 mg/1
Cadmium	.02	.05	.46	.87	.82
Chromium +6					
Chromium Total	1.11	5.7	2.36	.36	.88
Copper	1.13	.32	1.24	2.56	.93
Cyanide Total	.52	1.0	.04	5.6	1.7
Iron					
Lead	.58	<.05	.05	.05	.06
Nickel	.32	1.86	1.32	.45	1.53
Silver	.072	<0.025	<0.025	<0.025	<0.025
Zinc	1.45	4.06	2.6	2.34	2.8
Total Metals	4.68	11.99	8.03	6.63	7.02
Total Tox Organics	2.13--------------		as TCE	0.18	----------
pH	5 ->10	6.1	4.5	9.3	8.06
Total Susp Solids					

Table 3
Confirmatory Test Results for Wastewater Characteristics

Parameter	Results
Chloride	0.99 mg/l
Sulfate	14.8 mg/l
Fluoride	<0.1 mg/l
Phosphate (Total) as PO4	0.21 mg/l
Cyanide (Total)	1.0 mg/l
Cyanide (Ammenable to Chlorination)	0.04 mg/l
Metal Total Basis:	
Aluminum	1.3 mg/l
Cadmium	0.035 mg/l
Calcium	6.90 mg/l
Chromium Total	9.20 mg/l
Chromium-Hexavalent	5.48 mg/l
Copper	0.41 mg/l
Iron	1.26 mg/l
Lead	0.10 mg/l
Magnesium	0.065 mg/l
Nickel	2.95 mg/l
Sodium	25.0 mg/l
Tin	<1. mg/l
Zinc	1.065 mg/l

Methodology: Methods for Chemical Analysis of Water and Waste, EPA- 600/4-79-020, March, 1983.

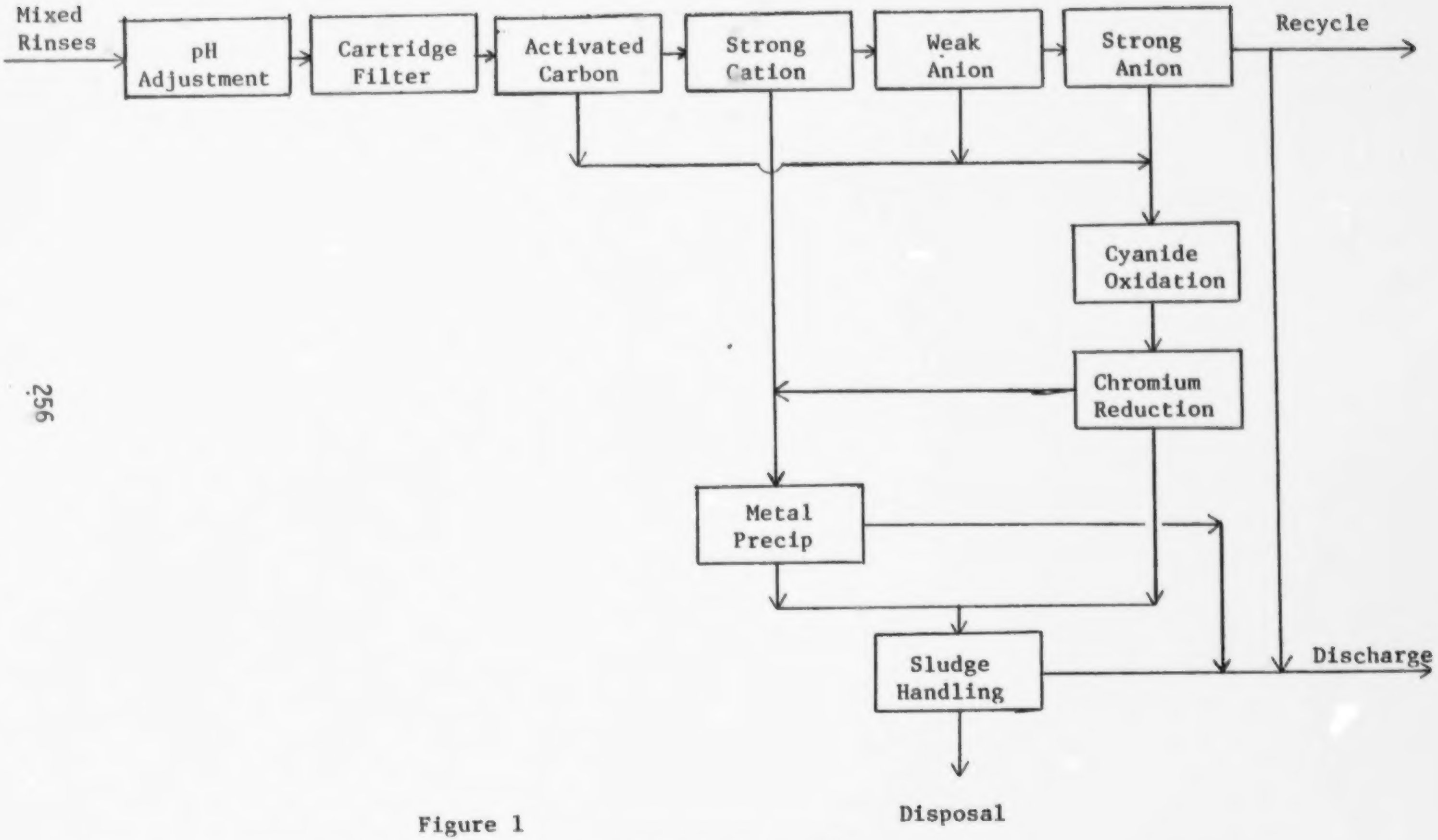
Mixed Rinses
pH Adjustment
Cartridge Filter
Activated Carbon
Strong Cation
Weak Anion
Strong Anion
Recycle
Cyanide Oxidation
Chromium Reduction
Metal Precip
Sludge Handling
Discharge
Disposal

Figure 1

Block Flow Diagram of The Waste Treatment/Recycle System
International Chromium Plating Company

ENVIRONMENTAL AUDITING: MANAGEMENT'S KEY TO EFFECTIVE ENVIRONMENTAL COMPLIANCE

By

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I. Introduction

Environmental auditing can be management's key to effective environmental compliance by assessing ones status with a myriad of changing regulatory requirements. Since environmental auditing activities represent a relatively new technique for industry, the definition and methods of conducting an environmental audit may vary significantly. The generally accepted definition used by the United States Environmental Protection Agency (EPA) defines an environmental audit as a: "systematic, documented, periodic and objective review of facility operations and practices related to meeting environmental requirements". This paper will present some of the reasons for performing an environmental audit, outline the basic procedure for performing an audit, and summarize problem areas-deficiencies frequently identified during audits of manufacturing facilities.

II. Why Conduct an Environmental Audit?

Environmental auditing can help management to identify policies and procedures which can have an adverse impact on a company's image or which may result in legal action by environmental groups or regulatory agencies, that could result in long-term financial, personal civil or criminal liability. A good corporate image takes years to establish--but can be rapidly and severely damaged by adverse publicity resulting from environmental lawsuits, hazardous material spills, or employee injuries or illness. An objective evaluation of company activities however, can provide management with the information needed to identify and help prevent these occurrences. An environmental auditing program can serve as an example of a "good neighbor" attitude on the part of facility management, and thus may improve public and employee relations.

Civil legal action by environmental interest groups has increased dramatically in the last three years. In many cases, companies subject to these citizen suits were, at the time, working constructively with state or Federal regulatory agencies to correct deficiencies and attain compliance with one or more specific requirements of an existing permit. Company management may be lulled into a sense of security due to a positive relationship with a regulatory agency, and may not realize that it still may become the subject of a citizen-third party suit. An effective environmental audit can draw management attention to non-compliance situations which are in the public record and therefore subject to discovery by environmental groups.

An environmental audit can help to prepare company management for "the real thing": inspection by a regulatory agency. The audit report should identify deficient practices which, if not corrected, could lead to enforcement by Federal, state and local agencies. This is particularly important for those practices which are subject to regulations enforced by state agencies which have the power to assess administrative penalties (i.e. without the need to file a civil law suit against a company). In these cases, it is absolutely critical that management identify and correct the problem before the regulatory agency becomes involved. There are certain cases, however, where notification of the regulatory agency is required prior to correcting the problem which has been discovered during the audit. Where notification may be required, the company's obligations should be discussed with legal counsel prior to such notification.

Environmental auditing can result in the identification of spills and leaks which may have occurred or are occurring. The audit can also aid to prioritize the prevention of events which have the potential to occur. Companies are now finding that the cost of cleaning up contamination on their property is far greater than the initial cost of proper chemical/waste management. Once a contaminated site has been identified, transfer of real estate becomes near impossible until completion of appropriate soil and groundwater clean-up which usually takes many years.

The exposure of company directors, officers and managers to personal civil or criminal liability has increased due to the recent enforcement emphasis by EPA and state agencies. In the past five years, EPA has increased its criminal investigation staff from one person located in Washington, D.C. to over fifty personnel with offices in each EPA region. The Department of Justice has similarly increased its staff of attorneys specializing in criminal prosecution for violation of Federal environmental statutes. On the state level, criminal indictments over the past three years have ranged from negligence to murder. In one recent case in the State of New Jersey, a company president was indicted on charges which could carry a maximum sentence of fourteen and one half years for "ordering" the disposal of one drum of nitric acid on company property.

Individuals have also been convicted of environmental crimes even when it could not be established that the officials knew the violations had occurred. The courts have ruled that responsible individuals "should have known" such violations occurred. Environmental auditing is thus an effective way for company management to learn what they "should know".

Audits may also be used to evaluate potential or actual liabilities of a potential business acquisition or merger. Information gained from an audit can be used to more adequately value the acquisition. The information can also be used during negotiations.

In some instances, the Securities Exchange Commission has required corporations to use environmental audits to develop information for public disclosure to stockholders. Insurance companies can also require, or initiate, audits of certain environmental activities as an additional component of traditional safety or loss-prevention audit programs.

III. EPA Environmental Auditing Policy Statement

EPA issued an environmental audit policy statement in the July 9, 1986, Federal Register. The information presented in this statement is a good starting point for companies interested in establishing an audit program.

EPA policy encourages the use of environmental audits. The policy also states EPA may require audits for "regulated entities" who have had a history of violations which were judged to result from inadequate environmental management, or where the nature of past violations indicate that similar non-compliance may occur at other facilities operated by the "entity".

As part of the environmental audit policy statement, EPA established what it considered to be the "elements" of an effective environmental auditing program. Two of the most important elements, according to EPA, were: that the audits have the support of top management, to help ensure that deficiencies noted during the audit would be addressed in a timely manner; and that the audit be performed by individuals who are independent of the activities being audited. Other critical elements, according to EPA, are that the auditing activity be a structured process to collect, analyze, interpret and document information, and that a written report be prepared summarizing the audit findings.

IV. Getting Started: Establishing Objectives, Scope and Project Team

Before undertaking an environmental audit, company management should carefully define the objectives of the audit. The most basic objective should be to determine compliance status with administrative requirements of environmental regulations to include such items as permits, reports, notifications and other documentation. This objective is a good first step, particularly for a small company.

A more aggressive objective for an environmental audit would be to review not only compliance status at one point in time, but also to review established environmental management policies and procedures. This objective allows management to project whether the company will be able to remain in compliance.

The most aggressive objective of an environmental audit would be to review compliance status and management practices, plus assess environmental risk(s) associated with activities which are presently regulated or which may result in environmental liability despite the absence of regulation at the time of the audit.

Once management has decided what the objectives of the environmental audit will be, the next step is to define the scope of the audit. The audit could address one or more selected facilities within a corporation or, for a smaller company, a selected process or area within a facility. The scope could also be limited to assessment of compliance with regulations of a particular discipline such as hazardous waste management, water pollution control, hazardous material storage, occupational health or safety, etc.

The scope of the audit is often affected by the amount of time required to perform the audit, the availability of in-house personnel or outside consultants to assist with the audit, and economic considerations. The impact of these considerations on the overall audit program can be minimized by implementing the program in a phased manner, over several years, with the scope of the audit increasing each time it is performed.

Once the objectives and the scope of the audit have been established, an audit team is assembled. The team can consist of one or more individuals who must be objective, plus have knowledge of the facility, processes, and applicable regulations. Often there is no one person who can meet all of these qualifications. It is not absolutely essential that every member of the audit team be independently objective, in fact it is usually necessary to have facility employees on the project team to help provide information on processes and records. For larger corporations, often there are employees who are familiar with a facility even though they do not work at the facility. One or more members on the team should be familiar however, with the specific type of processes performed at the facility so that all activities associated with that process can be adequately reviewed, and no potential problems overlooked.

Knowledge, understanding and experience of the technical aspects of regulations is perhaps the most difficult qualification required. It will often be necessary to rely on an outside consultant who has been able to remain up-to-date with regulatory requirements. The presence of an outside consultant on the audit team also helps to ensure the objectivity of the team.

The final qualification which may be required is knowledge of the legal implications and impacts of environmental laws. This is particularly critical where it is possible that criminal liabilities exist. By using legal counsel to direct and review the audit it may be possible to protect the results of the audit from legal discovery by regulatory agencies via the establishment of a client-lawyer privileged relationship. Legal counsel could also provide valuable recommendations regarding the legal responsibilities of company management when faced with potential environmental liabilities.

V. Performing the Audit

Certain activities must be performed prior to the audit site visit. Typically, information regarding the facility (including site plans, process operations and chemistry, permit applications and permits, reports, correspondence with regulatory agencies, etc.) is collected via a questionnaire which is completed at the direction of the facility manager. Regulatory agencies which may have some jurisdiction over an activity at the facility are contacted by team members to verify that the regulations on hand are current, and to inquire about new programs which may be being put into effect. Facility-questionnaire information is reviewed in detail and activities which may be potentially regulated are noted.

An audit checklist or questionnaire is then prepared for use during the site visit. This checklist is carefully developed to help ensure efficient use of time spent at the facility. It is particularly useful to obtain checklists used by the appropriate regulatory agencies, as either references or for direct use during the site visit. The references listed are also helpful in developing complete questionnaires and checklists.

The audit site visit should be scheduled several weeks in advance to allow the team to adequately prepare and to ensure the site visit is performed on a typical operating day, with minimal interference with production. Members of the audit team tour the facility to verify information provided by facility management, observe operations, and to gather any other information which may impact the environmental compliance issues in the project scope. Documentation of compliance status is reviewed by examining company records. Depending on the predetermined scope, documentation reviewing may either consist of simple verification that the documents exist and are kept on file, or the review may include detailed analysis of a random sample to determine the correctness and completeness of the documents. If included in the scope, certain documents such as training manuals and management plans can be copied for review after the site visit.

Upon completion of the site visit, facility personnel are briefed regarding the more important findings of the audit. During preparation of the formal written audit report, facility personnel are kept appraised of the information which will be included in the report.

The product of each environmental audit is a report which states the scope of the audit (i.e. the processes and regulatory requirements reviewed), the areas of potential or actual non-compliance which were observed and, if desired, prioritizes the audit findings and compliance deficiencies. The report may not include a detailed description of how to achieve compliance or of the costs associated with achieving compliance: these are generally considered to be follow-up activities which should be performed after completion of the audit. Follow-up activities can often be carried out by existing facility staff, although assistance and/or guidance from an outside consultant may be required.

VI. Summary of Common Compliance Problems

Mabbett, Capaccio & Associates, Inc. has directed or participated in numerous environmental audits during the past several years. A review of the findings in these audits indicated that there were three basic problem areas which were common to many of the audited facilities: 1) lack of documentation/recordkeeping; 2) improper hazardous materials and waste handling; and 3) inadequate management procedures/training. Specific examples are presented to illustrate the types of deficiencies which may be encountered during an audit.

A. Lack of Documentation/Recordkeeping

An essential element to help protect against potential civil and criminal liabilities is the maintenance of complete records and documentation of environmental compliance activities. In most cases this documentation is required by law or regulation; in others it is just good business procedure or common sense. Due to the volume of documentation required to demonstrate compliance, and the numerous departments and personnel involved in generating the necessary documentation, an efficient system must be established. A duplicate filing system (consisting of a central file of all original documents to back-up numerous "working" files kept by personnel responsible for a particular environmental compliance activity) is helpful to properly manage documentation. Duplicate filing is particularly useful to help alleviate the problems often encountered due to personnel turnover.

The most serious documentation deficiencies are those which involve permits. Permits obtained are often specific to the process and equipment contained in the application, however modifications to process components and pollution control equipment are often made without obtaining additional written approval which is normally required by regulatory agencies.

Permit expiration dates, or deadlines for obtaining permits, often pass without renewal or issuance of permits. In some cases this is the result of delay on the part of regulatory officials, however it is common for companies to allow these deadlines to pass without obtaining written documentation from the regulatory agency that an extension has been granted.

In several cases the auditing effort revealed that facilities were performing activities which required permits, yet without knowledge that the permits were required. The most common examples were: hazardous waste recycling on-site which would require a hazardous waste treatment permit; extended storage of hazardous waste on-site discharge of industrial waste to leach fields or to the ground outside the facility without a groundwater discharge permit; and the use of a public water supply without a backflow prevention or cross connection control permit.

Reports submitted to regulatory agencies without confirmation that the reports have actually been received by the agency is another example of inadequate documentation. All reports should be sent by certified mail/return receipt requested or some other means wherein the company submitting the report has a permanent record that the report was received.

Most states require the submittal of a report of a spill incident even when the incident appears to be minor or below a Federal "reportable quantity". A common identified deficiency has been the failure to report such spill incidents due to misinterpretation of legal requirements.

Other reports which are frequently not filed included Federal pretreatment reports such as a baseline monitoring report, a ninety-day compliance report, and the semi-annual monitoring report. Hazardous waste annual reports and permit-mandated monitoring reports were typically being submitted as required, however, the content of the reports were sometimes not in full compliance with the requirements of the regulations or permit. Many companies have also failed to maintain proper and adequate accident and illness records as required by OSHA.

Internal recordkeeping was frequently determined to be deficient. Hazardous waste inspection logs, hazardous waste training records, wastewater treatment system operation and maintenance logs, wastewater treatment personnel training records and certification, hazard communication training records, and Material Safety Data Sheets are examples of internal recordkeeping which must be maintained in order to document compliance.

Another common deficiency has been the lack of a "written" hazard communication management program as required by the OSHA, Hazard Communication Standard, 29 CFR Part 1910.1200. Failure to develop and implement an adequate training program has also been noted on a frequent basis.

Internal records of hazardous material spill incidents (including spills during handling, leaks from underground storage tanks, etc.) were often found to be deficient. For example, reports did not adequately describe response and clean-up measures taken, or document, using laboratory data, the levels of contamination remaining in soil which was not removed from the site.

B. Hazardous Material and Waste Handling Practices

The second type of common problem identified during audits falls under the general heading of hazardous material and waste handling practices. The problems were frequently associated with shipping and receiving activities, storage activities, and in-process activities.

Small quantity spills or releases during shipping and receiving of chemicals and waste are often considered to be insignificant. Examples include drippings from tranfer hoses, and spills during transfer from bulk to small quantity containers. These drippings and leaks often are allowed to seep into the ground or accumulate in drip pans or other open containers for long periods of time. Auditors frequently noted that shipping and receiving areas were not designed to control large spills, and uncovered storm drains were located near the shipping and receiving area.

One other problem associated with "receiving" activities, which results in hazardous waste and OSHA hazard communication compliance difficulties, is receipt of unauthorized or off-specification chemicals or samples. These chemicals, if not put into use within a certain time period (which varies from state to state), become subject to hazardous waste regulation. Hazardous waste storage without adequate labeling, particularly in "satellite accumulation areas", was also a frequent finding.

Aboveground hazardous material and waste storage areas often do not meet either OSHA or state code requirements or good engineering design for flammable storage, spill containment, segregation, ventilation or separation from rainwater.

Underground hazardous material and waste storage was frequently being performed without routine tank and piping leak detection testing which may be required by certain current state or local regulations. Installation of leak detection systems for underground tanks and piping was also a common audit recommendation.

Inappropriate in-process handling of hazardous materials and transfer containers often resulted in violation of OSHA requirements, or presented unnecessary risks of injury. Unauthorized dumps of process chemicals often resulted in unnecessary wastewater treatment expense or upsets resulting in noncompliance. Spill containment trays or tanks, (under plating and etching tanks and associated pumps and filtration systems) were frequently recommended to prevent release of materials which inevitably leak or spill from this type of process equipment.

C. Management Procedures and Training

A third major area of concern commonly uncovered during environmental auditing, regards inadequate management procedures and training. In several cases written plans required by law or regulation had not been prepared, including oil spill prevention control and countermeasure (SPCC) plans, contingency plans, personnel training plans and written hazard communication programs. In some instances, written plans had been prepared, however the plans were not up-to-date and the required periodic training had not been performed.

Many of the common problems under the first two headings (documentation and recordkeeping, and hazardous material and waste handling) could have been avoided or corrected by development and implementation of proper management procedures including employee training and the establishment of effective and efficient internal communication and control functions.

VII. Environmental Auditing: A Component of an Effective Environmental Compliance Management Program

The result of an environmental audit is almost never a "clean bill of health" statement. Management should not review the results with a "pass" or "fail" attitude, but rather should accept the reality that environmental compliance can be an elusive goal which each facility should continually make good faith efforts to achieve. Management should keep in mind that they are not alone in their noncompliance problems, however, this fact should not result in a false sense of security. Follow-up must be performed to address the findings and recommendations presented in the audit report. Failure to implement appropriate follow-up and/or corrective actions can be viewed by regulators as serious willfull intent to avoid compliance under certain circumstances. Management should be committed to follow through from the beginning or the value of the audit program should be reconsidered.

Upon issuance of the audit report, findings should be evaluated and reported to top-level management. Deficiencies should be prioritized based on risk assessment and liability exposure. An internal compliance schedule should be established to address each area of concern. The internal schedule should be realistic, taking into account technical limitations or difficulties which will be encountered in attaining compliance, and the availability of resources (equipment, personnel and financial) required to attain compliance.

Regulatory officials should be notified of those audit findings for which notification is required by law. Determination of this requirement should only be made with the assistance of legal counsel. Finally, follow-up/periodic audits should be scheduled to help ensure continued regulatory compliance.

While environmental auditing was initially conceived by large corporations (typically petrochemical and chemical process industries), auditing has now received increased attention from management of smaller companies interested in protecting their long term profitability and minimizing corporate and personal liability exposure. Environmental auditing can be an extremely useful tool, enabling company management to obtain objective information required to form the basis of a sound environmental management program.

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OPTIMIZING TRANSFER EFFICIENCY OF SPRAY PAINTING OPERATIONS

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Introduction

Between 1984 and 1986, the U. S. EPA, Air and Energy Engineering Research Laboratory and its contractor, Centec Incorporated of Reston, VA, conducted an extensive test program to define the effects of operating and maintenance (O&M) practices on spray painting transfer efficiency (TE). Three different spray painting systems were used during the test program, including air atomized conventional, air atomized electrostatic, and airless conventional systems. Over 30 operating variables were initially identified and evaluated for testing. An experimental design was developed that defined the effects of each variable on resulting TE. Eight of the variables were identified as the most important system variables and received extensive testing where applicable. They included restricted air lines, booth air rates, gun cleanliness, restricted paint lines, fan or shaping air, gun tip erosion, electrode position, and tip voltage. The data analysis technique used to evaluate the data explored first- and second-order system responses as well as interactions between the parameters. Regressions were developed where possible to define the TE responses to O&M factors for each equipment type.

Although, intuitively the results of most experiments were obvious, the projects defined the magnitude and direction of impact of the O&M variables on TE. By understanding the impacts of O&M variables on transfer efficiency, both the design of equipment and painting facilities can be optimized to maximize painting efficiency and subsequently reduce pollutant emissions, the ultimate goal of this research activity. This paper will summarize the major findings of this research program. The complete results of this program can be found in EPA Report No. EPA-600/2-85-107, "Transfer Efficiency of Improperly Maintained or Operated Spray Painting Equipment Sensitivity Studies" (NTIS No. PB 86-108271).

Approach

O&M variables were defined for each equipment type through literature reviews, and industry and equipment manufacturer communication. Over 30 specific variables were identified as having the potential to influence TE. Based upon evaluation and study of each variable in the laboratory, the most significant of these were selected for testing. Up to seven variables were evaluated on a single equipment type.

The experimental design selected for each equipment type consisted of a fractional factorial design augmented by a star design and a set of replicates. The purpose of this type of experimental design is to permit altering of several variables simultaneously in such a way that the effect of an individual variable can be discussed rather than altering one variable at a time. This allows a significant decrease in the number of experiments required to collect comparable data. The star portion of the experimental design allows one to evaluate the extremes of the variable and assess the lack of fit for development of regression models. The resulting experimental design results in an nth degree matrix from which the regression models were developed.

The painting targets used during the program consisted of a bank of flat panels and vertical cylinders wrapped with aluminum foil. After each test run the foils were dried, removed from the target, and weighed. The target configuration is shown in Figure 1. The resulting TE value used for development of the regression models is defined by equation (1):

$$TE = \frac{\text{Weight Paint Solids Deposited}}{\text{Weight Paint Solids Sprayed}} \times 100\% \qquad (1)$$

Based on the measured TE results from each test run, regression models were constructed for each target configuration and gun type using the Statistical Analysis System (SAS).

During each experiment, deteriorated levels of each variable were selected by setting all variables except the subject variable at the base operating level. The subject variable was then altered until spray pattern degradation could be visually discerned. For variables with more than two operating settings, intermediate levels of degradation were calculated to be evenly spaced from the base level to the deteriorated level. Table 1 is an example of O&M variables defined for the air atomized conventional systems where level "a" or "1" defines the base level and level "-a" or "-1" denotes the deteriorated level of operation. Intermediate levels in Table 1 are denoted by "1," "0," and "-1" where applicable. Dummy variables (d_n) represent undefined and uncontrolled factors, and take values of 0 or 1.

Air Atomized Conventional

The variables for the air atomized conventional (AAC) tests are given in Table 1 and defined in the resulting regressions as:

X_1 = restricted atomizing air lines
X_2 = booth air rate (linear velocity)
X_3 = gun cleanliness
X_4 = restricted paint lines
X_5 = fan air (horn or shaping air)

The experimental design and assigned values of X_n are shown in Table 2. Because certain variables (i.e., X_3 and X_5) cannot be measured quantitatively, they are termed qualitative variables.

The regression model developed for AAC flat panel experiments is given in equation (2):

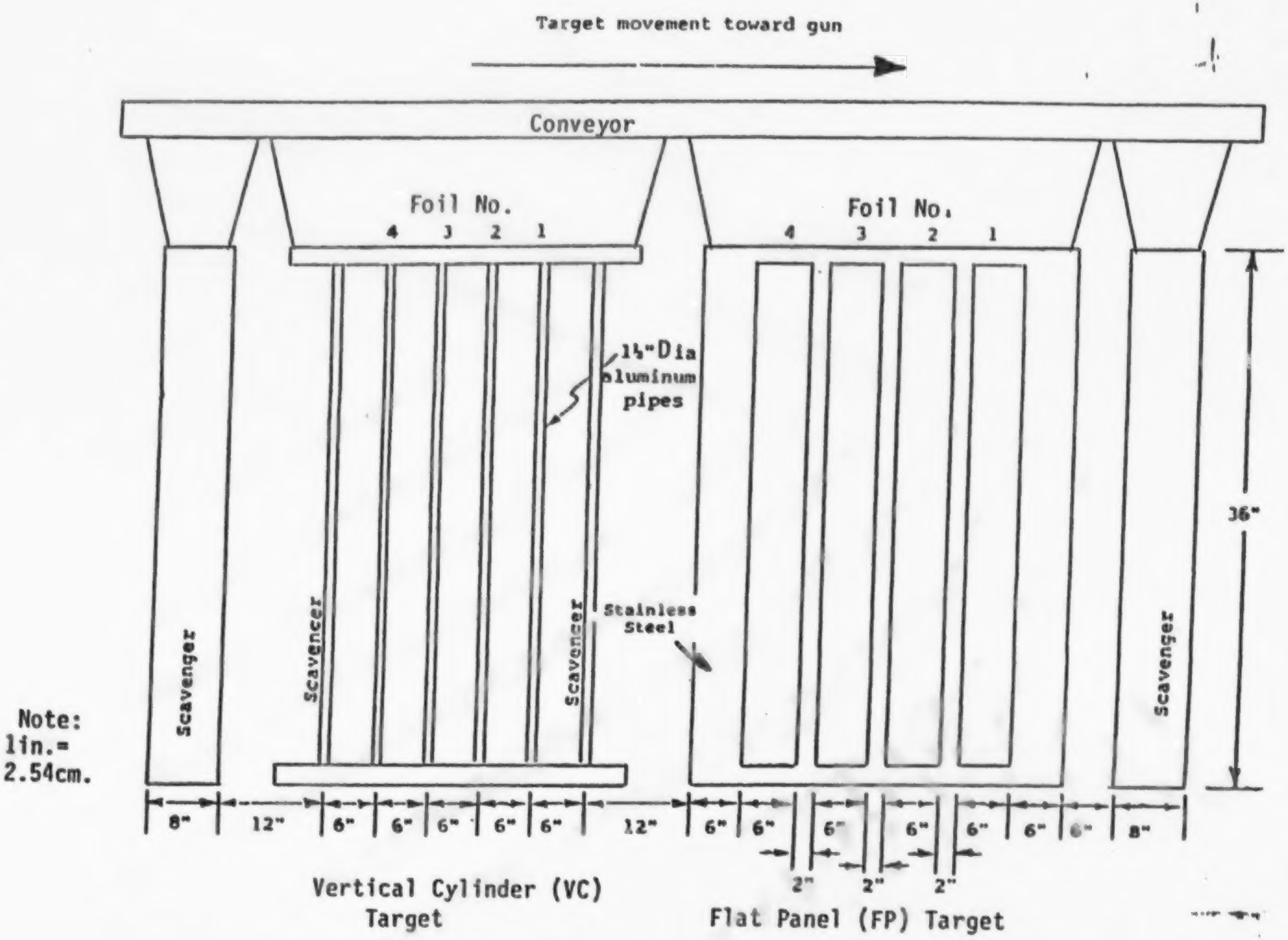
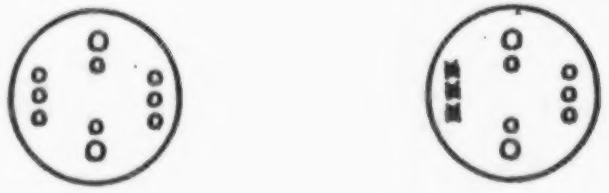

Target movement toward gun
Conveyor
Foil No.
4 3 2 1
Foil No.
4 3 2 1
1¼"Dia aluminum pipes
Stainless Steel
Scavenger
Scavencer
Scavencer
Scavenger
36"
8"
12"
6"
6"
6"
6"
6"
12"
6"
6"
6"
6"
6"
6"
6"
8"
2"
2"
2"
Vertical Cylinder (VC) Target
Flat Panel (FP) Target
Note: 1in.= 2.54cm.

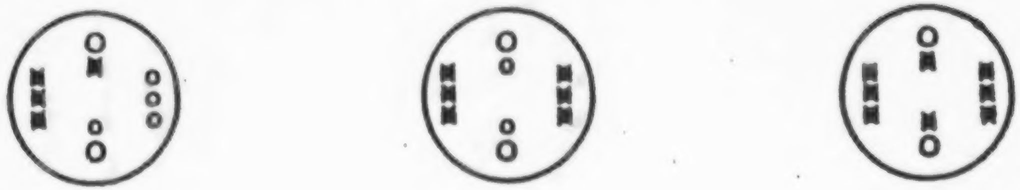
Figure 1. Target configuration for air atomized conventional and electrostatic spray guns.

TABLE 1. LEVELS OF OPERATING AND MAINTENANCE VARIABLES TESTED ON AIR ATOMIZED CONVENTIONAL SPRAY PAINTING EQUIPMENT

Variable	Quant./ Qual.	No. of Levels	Test Levels
Restricted atomizing air lines	Quant.	5	a = 239.0 kPa (20 psig) 1 = 218.6 kPa (17 psig) 0 = 197.9 kPa (14 psig) -1 = 177.2 kPa (11 psig) -a = 156.6 kPa (8 psig)
Booth air rate (linear velocity)	Quant.	2	1 = 0.61 m/s (120 ft/min) -1 = 0.36 m/s (70 ft/min)
Gun cleanliness	Qual.	5	See Figure 2
Restricted paint lines	Quant.	5	a = 180.7 kPa (11.5 psig) 1 = 170.3 kPa (10.0 psig) 0 = 160.0 kPa (8.5 psig) -1 = 149.7 kPa (7.0 psig) -a = 139.3 kPa (5.5 psig)
Fan air	Qual.	3	1 = wide open 0 = one turn shut -1 = two turns shut



Level +a; all holes open **Level +1; 3 holes plugged**



Level 0; 4 holes plugged **Level -1; 6 holes plugged** **Level -a; 8 holes plugged**

Figure 2. Air cap test levels for gun cleanliness

TABLE 2. AAC EXPERIMENTAL DESIGN

Run No.	X_1	X_2	X_3	X_4	X_5
1	-1	-1	-1	-1	1
2	-1	-1	-1	1	-1
3	-1	-1	1	-1	-1
4	-1	1	-1	-1	-1
5	1	-1	-1	-1	-1
6	1	1	1	-1	-1
7	1	1	-1	1	-1
8	1	1	-1	-1	1
9	1	-1	1	1	-1
10	1	-1	1	-1	1
11	1	-1	-1	1	1
12	-1	1	1	1	-1
13	-1	1	1	-1	1
14	-1	1	-1	1	1
15	-1	-1	1	1	1
16	1	1	1	1	1
17	-a	-1	0	0	0
18	a	-1	0	0	0
19	0	1	-a	0	0
20	0	1	a	0	0
21	0	-1	0	-a	0
22	0	-1	0	a	0
23	0	1	0	0	-1
24	0	1	0	0	1
25	a	1	a	a	1
26	a	1	a	a	1
27	a	1	a	a	1
28	a	1	a	a	1
29	a	1	a	a	1
30	a	1	a	a	1

Where:

X_1 = Restricted atomizing air lines--test at 5 levels: a,1,0,-1,-a

X_2 = Booth air rate--test at 2 levels: 1,-1

X_3 = Gun cleanliness--test at 5 levels: a,1,0,-1,-a

X_4 = Restricted paint lines--test at 5 levels: a,1,0,-1,-a

X_5 = Fan air--test at 3 levels: 1,0,-1

$$TE = 68.95 - 3.12X_1 - 0.98X_2 + 2.87X_4 - 1.16X_4^2 + 12.48X_5d_1 - 4.79X_5d_2 + 0.51X_1X_2 - 0.17X_2X_5d_1 \qquad (2)$$

As previously indicated, some of the results are intuitively expected; thus an analysis of the regression model confirms what was expected. For example, the negative coefficient of X_1 indicates, as expected, a tendency for TE to decrease with an increase in the degree of restriction of the atomizing air lines. Similarly, an increase in booth air rate (X_2) indicates that the TE will continue to decrease with increasing booth air velocity. Increases in the degree of paint line restriction (X_4) will increase TE, but the amount of increase approaches a constant value as the level becomes larger. The mixed coefficients of the fan air variable (X_5d_n) suggest that TE changes significantly as the fan air control is changed from the full open optimum position to the partially shut degraded position. The mixed term X_1 X_2 indicates that there is an interaction between the atomizing and booth air rates that can impact TE in a positive or negative manner depending on the defined level of each.

The TE regression model for the AAC system on vertical cylinders is shown in equation (3):

$$TE = 11.99 - 0.91X_1 - 0.28X_2 + 0.44X_4 + 2.38X_5d_1 \qquad (3)$$

The negative coefficients of atomizing air (X_1) and booth air rate (X_2) indicate that TE decreases with increases in atomizing air pressure and booth air rate, respectively. Fan air (X_5d_1) has a significant impact at its most degraded level. In fact the effect of degraded fan air outweighs all other evaluated variables combined.

It is interesting to note the absence of the gun cleanliness variable (X_3) in this model. This surprising result goes against conventional expectations of normal gun operation and maintenance.

AAC Test Conclusions

The regressions for the flat panel and vertical cylinder targets presented illustrate the differences that target configuration can make in TE. Even with these differences, however, there are basic consistencies between the results. Three variables (restricted atomizing air lines, restricted paint lines, and fan air) were identified as significant for both target configurations. A fourth variable, booth air rate, was significant for the first panel targets. The consistency of these results strongly implies that these four factors have a critical influence on TE regardless of target configuration.

Thus, selection and maintenance of appropriate atomizing air pressure and paint pressure should be given regular attention by the operator. Fan air rates have the strongest influence on TE for the two target types, as demonstrated by the large coefficient in each of the regressions. Fan air levels are often set by individual operators according to their own judgment. For optimum TE, plant management should determine optimum spray painting conditions through test runs and then specify those conditions for the operator.

The absence of the gun cleanliness variable indicates that the paint that is ejected from the gun is used more effectively. The point of ejection from the gun nozzle does not adversely affect the spray pattern which is controlled by more dominant variables. Some reevaluation of booth air-rates may be justified by the test results, which indicate that the lowest level of booth air rate should be selected to maximize TE. However, one must take into account applicable safety regulations, as well as provide for worker comfort when considering lowering booth rates. The regressions can be used to estimate the change in TE that can be expected and the magnitude and direction of the change caused by the specific variable.

Air Atomized Electrostatic

Seven variables were selected for the experiments on air atomized electrostatic equipment. These variables included:

X_1 = restricted atomizing air lines
X_2 = booth air rate (linear velocity)
X_3 = gun cleanliness
X_4 = restricted paint lines
X_5 = fan air
X_6 = tip voltage
X_7 = electrode position

Table 3 shows the levels at which each variable was tested. The experimental design is presented in Table 4.

The regression model developed for the air atomized electrostatic system on flat panel targets is defined in equation (4):

$$TE = 94.72 - 2.27X_1 + 1.56X_4 + 1.22X_6 - 3.05X_1d_1 \tag{4}$$

The equation indicates that, for those variables appearing in the model, all must be considered significant. The negative coefficients of atomizing air (X_1) and electrode position (X_7) indicate a drop in TE as each variable is increased, respectively. The positive coefficients of the restricted paint lines (X_4) and tip voltage (X_6) indicate that TE increases with increasing values of each variable.

The regression model for the AAE vertical cylinder experiments is defined in equation (5):

$$\begin{aligned} TE = {} & 41.34 - 1.11X_1 - 2.66X_2 - 2.33X_3d_3 + 2.46X_4^2 \\ & - 8.20X_5d_1 + 6.71X_6 - 0.99X_6^2 \;\; 18.25X_1d_2 + 1.82X_2X_5 \end{aligned} \tag{5}$$

TABLE 3. LEVELS OF OPERATING AND MAINTENANCE VARIABLES TESTED ON AIR ATOMIZED ELECTROSTATIC SPRAY PAINTING EQUIPMENT

Variable	No of Levels	Test Levels
Restricted atomizing air lines	5	a = 293.0 kPa (20 psig) 1 = 218.6 kPa (17 psig) 0 = 197.9 kPa (14 psig) -1 = 177.2 kPa (11 psig) -a = 156.6 kPa (8 psig)
Booth air rate (linear velocity)	2	1 = 0.61 m/s (120 ft/min) -1 = 0.36 m/s (70 ft/min)
Gun cleanliness	5	See Figure 2.
Restricted paint lines	5	a = 180.7 kPa (11.5 psig) 1 = 170.3 kPa (10.0 psig) 0 = 160.0 kPa (8.5 psig) -1 = 149.7 kPa (7.0 psig) -a = 139.3 kPa (5.5 psig)
Fan air	3	1 = wide open 0 = one turn shut -1 = two turns shut
Tip voltage	5	a = 72 kV 1 = 63 kV 0 = 54 kV -1 = 45 kV -a = 36 kV
Electrode position (See Figure 3)	3	1 = normal 0 = best -1 = clipped off

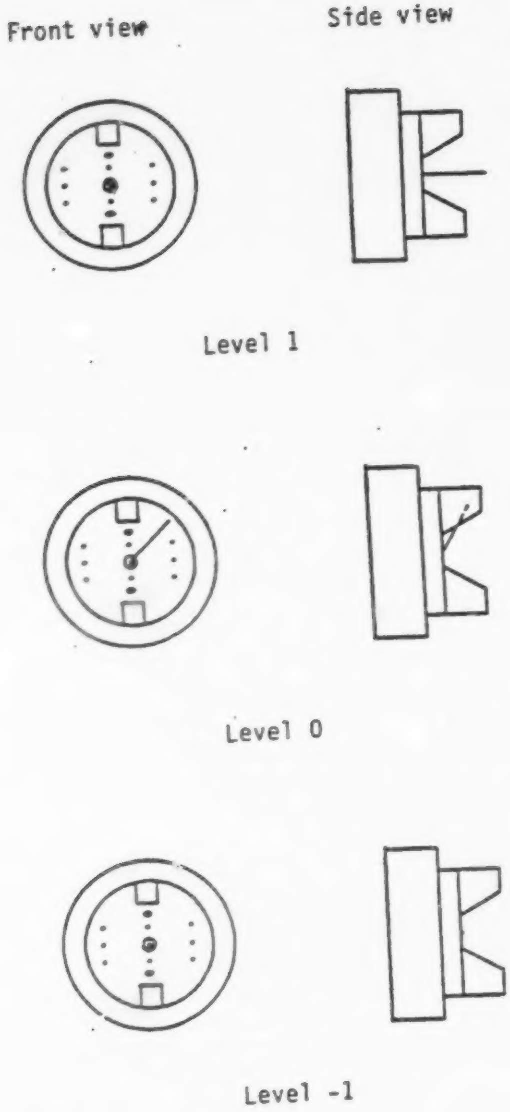

Front view
Side view
Level 1
Level 0
Level -1

Figure 3 Air atomized electrostatic electrode position test levels

TABLE 4. AAE EXPERIMENTAL DESIGN

	Variable						
Run No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7
1	-1	-1	-1	-1	-1	-1	-1
2	1	1	1	-1	-1	-1	1
3	-1	-1	-1	1	1	1	-1
4	1	1	1	1	1	1	1
5	1	-1	-1	1	1	-1	1
6	-1	1	1	1	1	-1	-1
7	1	-1	-1	-1	-1	1	1
8	-1	1	1	-1	-1	1	-1
9	-1	-1	1	-1	1	-1	1
10	1	1	-1	-1	1	-1	-1
11	-1	-1	1	1	-1	1	1
12	1	1	-1	1	-1	1	-1
13	1	-1	1	1	-1	-1	-1
14	-1	1	-1	1	-1	-1	1
15	1	-1	1	-1	1	1	-1
16	-1	1	-1	-1	1	1	1
17	-a	-1	0	0	0	0	0
18	a	-1	0	0	0	0	0
19	0	1	a	0	0	0	0
20	0	1	-a	0	0	0	0
21	0	-1	0	-a	0	0	0
22	0	-1	0	a	0	0	0
23	0	1	0	0	-1	0	0
24	0	1	0	0	1	0	0
25	0	-1	0	0	0	-a	0
26	0	-1	0	0	0	a	0
27	0	1	0	0	0	0	-1
28	0	1	0	0	0	0	1
29	a	1	a	a	1	a	1
30	a	1	a	a	1	a	1
31	a	1	a	a	1	a	1
32	a	1	a	a	1	a	1
33	a	1	a	a	1	a	1
34	a	1	a	a	1	a	1

Where:

X_1 = Restricted atomizing air lines--test at 5 levels: a,1,0,-1,-a
X_2 = Booth air rate--test at 2 levels: 1,-1
X_3 = Gun cleanliness--test at 5 levels: a,1,0,-1,-a
X_4 = Restricted paint lines--test at 5 levels: a,1,0,-1,-a
X_5 = Fan air--test at 3 levels: 1,0,-1
X_6 = Tip voltage--test at 5 levels: a,1,0,-1,-1
X_7 = Electrode position--test at 3 levels: 1,0,-a

This experimental scenario indicates that several factors are significant in the resulting TE. As in the flat panel case, the negative coefficient of X_1 indicates that, as air pressure increases, the resulting TE decreases. Similarly, the negative coefficient of X_2 indicates that, as both air rates increase, the TE decreases. This effect, however, can be moderated by the interaction of booth air rate (X_2) with fan air (X_5). Restricted paint lines (X_4) are quadratically significant with a positive coefficient indicating that an increase in paint pressure also increases TE.

A significant surprise were the results of the gun cleanliness experiments. In only one instance (level +1, as defined in Figure 2) is there a significant impact on apparent TE. This result goes against conventional expectations. It does not suggest, however, that normal gun cleaning during maintenance is not important; rather, it suggests that this maintenance will typically have less impact on consistently high equipment efficiency than other O&M practices, except in extreme cases.

Airless Conventional

Test variables selected for testing during the airless conventional (ALC) experiments included booth air rate, tip erosion, and restricted paint lines. Table 5 gives the range and levels of testing for each variable which are defined below.

X_1 = booth air rate
X_2 = tip erosion
X_3 = restricted paint lines

The experimental design is shown in Table 6.
The regression model for the flat panel targets is given in equation (6):

$$TE = 74.4 - 5.47X_2 - 1.94X_2^2 \tag{6}$$

The only significant variable identified during these experiments was tip erosion. Tip erosion was simulated during the experiment by using progressively larger tip hole diameters. The negative coefficients of the X_2 terms show that, as tip erosion progresses, the apparent TE decreases.

The regression model for the vertical cylinder experiments, equation (7), indicates that tip erosion (X_2) is the only significant variable found to affect TE for ALC equipment.

$$TE = 12.90 - 1.4X_2 - 0.78X_2^2 \tag{7}$$

ALC Conclusions

Three O&M variables were selected for testing on ALC spray painting equipment: tip erosion, booth air rate, and restricted paint lines. In every test case, tip erosion was the overwhelming variable affecting TE.

The tremendous response to changes in tip diameter is indicative of a very strong relationship between selection of appropriate tip diameter and TE. This would indicate that tip diameter should be carefully selected and maintained for the particular job requirement.

From the data generated during this test program, very little can be said about the effects of other variables on TE for ALC spray systems. The response of TE to tip erosion is so overwhelming that it possibly obscures other potentially important variables.

TABLE 5. LEVELS OF OPERATING AND MAINTENANCE VARIABLES TESTED ON ALC SPRAY PAINTING EQUIPMENT

Variable	No. of Levels	Test Levels
Booth air rate (linear velocity)	2	1= 0.61m/s (120 ft/min) -1= 0.36m/s (70 ft/min)
Tip erosion*	5	a= 0.28 mm (0.011 in.) Tip dia. 1= 0.28 mm (0.011 in.) Tip dia. 0= 0.33 mm (0.013 in.) Tip dia. -1= 0.38 mm (0.015 in.) Tip dia. -a= 0.38 mm (0.015 in.) Tip dia.
Restricted paint lines	5	a= 9066.9 kPa (1300 psig) 1= 8377.2 kPa (1200 psig) 0= 7687.6 kPa (1100 psig) -1= 6997.9 kPa (1000 psig) -a= 6308.3 kPa (900 psig)
Dummy	3	1, 0, -1

* Tip erosion simulated by changing tip diameter. Only three tip diameters used.

TABLE 6. ALC EXPERIMENTAL DESIGN

Run No.	Variable X_1	X_2	X_3	Dummy
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	-1	-1	1	-1
5	-1	-1	-1	1
6	1	1	-1	-1
7	1	-1	1	-1
8	1	-1	-1	1
9	-1	1	1	-1
10	-1	1	-1	1
11	-1	-1	1	1
12	1	1	1	-1
13	1	1	-1	1
14	-1	1	1	1
15	1	-1	1	1
16	1	1	1	1
17	1	-a	0	0
18	1	a	0	0
19	-1	0	-a	0
20	-1	0	a	0
21	1	0	0	-1
22	1	0	0	1
23	1	a	a	1
24	1	a	a	1
25	1	a	a	1
26	1	a	a	1
27	1	a	a	1
28	1	a	a	1

Where:

X_1 = Booth air rate--test at 2 levels: 1,-1
X_2 = Tip erosion--test at 3 diameters: 0.28, 0.33, 0.38 mm
X_3 = Restricted paint lines--test at 5 levels: a,1,0,-1,-a
Dummy = 1,0,-1

General Conclusions on the Effects of Operating and Maintenance Variables on TE

AAC transfer efficiency was most strongly affected by restricted air lines. This effect was pronounced over the two target types tested and should be considered the most prominent O&M variable tested for this type of spray system. Fan air adjustments also had a strong effect and should be considered a major effect as well. Restricted paint lines and booth air rates had significant effects, although not as strong as restricted air lines or fan air.

AAE transfer efficiency was affected by the highest number of variables. The most prominent effect was voltage, followed by restricted air lines and restricted paint lines. Booth air, fan air, and electrode position also had significant effects.

ALC transfer efficiency was overwhelmingly affected by tip erosion.

It is important to note that, although the regression models confirmed most expectations of the impact of most O&M variables on TE, they also indicate that certain variables are less important than one would believe. For example, booth air rate did not exhibit the impact on TE across the scenarios tested as might be intuitively expected. Only for the air atomized conventional and electrostatic vertical cylinder experiments was booth air rate determined significant to total TE. A second surprising finding was the lack of influence on overall TE of gun tip cleanliness, simulated by restricted nozzle holes. At most, this qualitative variable exhibited only moderate impact on TE for the systems tested. This indicates that, unless painting quality is adversely impacted, less care needs to be taken on tip cleanliness than for other O&M variables for the guns.

The results of this program indicate that the relative importance of each variable for a certain target configuration should be given individual consideration by plant management. Laboratory test runs, made with plant paint and workpiece targets, should determine optimum combinations of factor levels that result in acceptable product finish and optimum transfer efficiency.

The program also proved the ability to model the operation of a spray painting facility and equipment. This capability to model the operation of a spray painting facility also allows the definition of facility modifications and manufacturing standards which will maximize TE.

The regression models developed during this program can serve as guidelines in setting up site specific tests to develop exact models for an individual facility. However, if such tests are impractical, these models can serve as guidelines for maximizing TE since they are directionally consistent for respective spray systems and conditions. They will not give, however, exact values of TE for specific sites.

SUCCESSFUL IN HOUSE RECOVERY OF SOLVENT

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Prices of solvents have increased, and will continue to increase dramatically, since the early 1970's. Legislation by federal and state governments have given "cradle to grave" responsibility to users of industrial solvents thereby causing cost of disposal to sky rocket. Solvents are essential to industrial processes, thus causing higher and higher costs of goods sold.

In order to cope with these ever increasing purchase costs, and expense and liability of disposal, hundreds of companies (many of them decorators and suppliers to the decorating industry) have opted to reclaim their contaminated solvents inhouse.

True solvent reclamation is achieved by distillation, not by mere filtering. Filtration alone may extend a solvent's life for a limited time. By removing particles such as metal shavings, dirt, etc., it can produce a reusable, although not pure solvent. Typically, parts washers come with a built-in filtering system to allow multiple uses of the solvent before a change is necessary. But filtration cannot extend its life indefinitely.

Distillation can return cleaning solvents to their original performance by removing all contamination, both suspended and dissolved. However, fractional distillation systems for breaking down solvents into their original components are expensive and not normally practical or necessary for reclaiming solvent for cleaning purposes.

Simple distillation units can reclaim both single and multiple component solvents. With multiple component solvents, composition may change due to evaporation during use. Normally, this will have little or no effect on utility of the distilled solvent because all properties necessary for cleaning are retained.

This article discusses solvent recovery with simple batch, package units. Equipment of varying capacities is readily available from several manufacturers, allowing the convenience of an innouse operation while substantially reducing both cost and hazardous waste disposal.

Distillation systems have not always been economically feasible for a business generating small quantities of waste solvent. One reason was that it was very expensive to design and manufacture a "safe" unit.

Underwriter's Laboratories states, "The maximum acceptable temperature for external surface of the heater for Class I, Group D, shall be 365° F." (Book UL823). This is by far the most important safety design aspect of a small distillation unit. Prior techniques used bayonet-type heaters immersed into a heat transfer fluid that in mis-operation could be disastrous and ultimately result in degradation of the fluid.

With small package batch distillation systems now available, electric heaters are cast into a heavy aluminum disc in the bottom of the distillation pot whose wall is also aluminum. Thus, the vessel is essentially a single piece of aluminum. The aluminum conducts the heat throughout the very thick bottom and up the walls in the contaminated solvent, transferring heat from almost all directions. The very thick cast bottom of this vessel and the cast-in thermowells with redundant temperature controllers prevent the temperature from exceeding 350° F. Also, it is absolutely necessary that the remainder of the unit be explosionproof -- this means full compliance with Class I, Group D, Division 2 of the National Electric Code. This adds some strict, difficult and costly requirements such as rigid conduits, special heavy electrical boxes, potted fittings, etc.

Many common and relatively inexpensive solvents such as mineral spirits boil at temperatures in excess of 365° F. Thus, they cannot be reclaimed "safely" (in compliance with UL) with a conventional unit of this type. To satisfy this need, a vacuum system attachment can be provided to allow distillation to occur at less than 365° F.

A secondary characteristic of this type system is the ability to solidify distillation residue/bottoms. By evaporating and recovering all volatiles, a solid or semi-solid residue is left that can meet RCRA landfill criteria. The process can recover volatiles from cleanup and mask-wash solvents, paint (including off-specification paint), spray booth sludges, and similar organic types of waste. It can also be used to purify vapor degreasing solvent.

Small-scale solvent recovery systems have evolved from conventional batch stills which required considerable effort in removing sludge and still bottoms. The evolution to a plastic disposable liner bag system was a clear step forward. In this process, a bag of high-temperature stabilized nylon film is inserted into the still to contain all solvent and residue. Solid, paste or liquid residues can then be removed simply by lifting out the bag. In most cases, the bag works well, but in some applications there is a physical degradation of the bag due to chemical attack and/or heat. A second disadvantage to the disposable bag is its cost -- as much as $500-1,000 per year.

An improvement to the liner bag feature is available with the introduction of small-batch solvent recovery units with a Teflon* coated boiling vessel. The residue remains behind in the pan and is easily removed by lifting out the pan.

For small batch distillation (15-55 gallons per shift), the boiling vessel is heated via electric heating coils encapsulated in the cast floor of the all-aluminum vessel. For large batch (or continuous) distillation (30-80 gallons per hour), a steam-heated jacket surrounds the distillation chamber. In either case, vaporized solvent is condensed in a water-cooled heat exchanger and collected in a receiving drum.

*Teflon is a Du Pont registered trademark.

In-house solvent recovery by batch distillation is rapidly gaining favor. Not only have prices of solvents increased dramatically, but disposal costs have, in some cases, gone from zero (or sometimes even payment for waste solvents) to $1-1.50/gallon. In some states, it is almost impossible to dispose of used solvents due to the lack of hazardous waste disposal sites.

Equipment available for less than $6,000 can recover about 15 gallons per shift. Such operations typically require a half hour of semi-skilled labor per shift and use 7-10¢ of electricity per gallon processed. When solvent cost plus disposal cost is considered, payback can be less than one year, even for single shift operations.

CASE STUDIES:

1. Degreasing Solvents

Following punching, welding and grinding of sheet and reinforcing steel in the manufacture of custom-built luminaires, a Pennsylvania company employed a degreaser for removal of surface oil.

Solvent prices were rising, and disposal of dirty solvent as hazardous material cost $90/drum. The once-through system for solvent use was proving too expensive.

Handcrafted workmanship is of a high order and use of dirty solvents in the degreaser, which leave a residue on the product, cannot be tolerated. They decided to find an alternate to adding new solvent to the degreaser every time a recharge was necessary.

Opting for in-house reclaiming, they installed a 15-gallon batch still which separates the volatile solvent from the oil picked up in the degreaser. Distilled solvent is collected in a drum for reuse, and the oil is retained as residue.

In the first year of operation, this Pennsylvania company experienced a reduction of more than 90% in new solvent purchase and also found reuse for the residual oil. Payback time also was approximately one year.

A one-shift, 15-gallon batch, daily distillation permits emptying the 160-gallon degreaser as often as once every two weeks, although with light contamination, this may be extended to once every 30 days.

2. Coating Manufacturers

Solvent recovery has been a necessary part of operations at a varnish company in Indiana. The plant needs to recover about 500 gal/day of a mixture of virtually all types of organic solvents:

- Ketones, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and acetone comprise roughly half the total.

- Aliphatic and aromatic solvents such as toluene, xylene, heptane, and naptha account for about 35% of the solvent mixture.

- Glycols, ethers, and alcohols represent the remaining solvent load.

This mixture of solvents has been calculated to cost approximately $2.16/gal.

The spent solvent needs to be treated primarily to remove accumulated water, and also to extract small amounts of pigment and other high boiling impurities. They had employed an extraction/recovery still that could process up to 30 gal/hr.; however, it required too high an operator skill level for the still to be economical.

Since the solvent was both too costly and too hazardous to discard, the plant contracted to have the spent solvent treated and returned. Along with the high cost, the purified solvent that was returned was of lower quality because the contractor would mix it with other solvent wastes before treatment. After investigating possible alternatives, a sample of the contaminated solvent was presented to a recovery still manufacturer for a feasibility determination. The results were favorable and warranted installation of an automated 500 gal/shift solvent distillation and recovery unit.

The solvent recovery equipment employs differential heat transfer technology. This is achieved by indirect heating through a jacket having bands of steam coils. By controlling the fluid level, temperature and viscosity, the solvent is separated by vaporization and is subsequently recondensed for recovery.

Contaminated solvents are collected in drums and unloaded into a holding tank prior to treatment. The solvent distillation unit automatically feeds from the tank. Continuous internal mixing and scraping in the distillation boiler keeps the feed in suspension and prevents residue buildup. The purified solvent is gravity discharged into a collection tank.

The automatic operation was an important deciding factor for the plant. Not only does it circumvent the problem of insufficient operator skill level, but it allows the person responsible for the unit's operation to do other functions; he performs the necessary material handling operations such as collection of contaminated solvent drums.

The recovery still was installed in January 1982 and has been operating with no major difficulties.

The unit is operated during one shift each day, reclaiming about 400-500 gallons of solvent and producing about one drum of still bottoms. According to daily logs, the cost of recovery has been $0.30-0.50/gal. compared to $1.05/gal charged for contract work. The payback period, based on these figures and including equipment and labor considerations, is estimated to be under two years.

Maintenance and operator requirements have been minimal. When the recorded solvent output level drops, the unit is washed (to clean heat transfer surfaces) and the scrapers are replaced.

The distillation unit has satisfactorily processed the spent solvents to an acceptable purity level. Analytical testing of the recovered solvents by gas chromatography has shown that the water content is less than 1% (no water peak detected).

3. Silk Screen Decorators

Early in 1982, a New England company saw a need to improve their screen cleaning process.

The existing system utilized a totally exhausted booth into which a hose washed down the contaminated silk screens. This not only created a liquid waste, but also vented thousands of dollars a year into the atmosphere. Their first step to improve the process and save money was to install an automatic screen washer. This washer is totally enclosed allowing no vapors to atmosphere during the cleaning process. The equipment saves 200 gallons per day of an extremely volatile MEK while extending its life up to 5 times before it needs changing.

Now having improved the washing process, a short time later a solvent still was purchased to reuse the waste solvent. Fifteen gallons are processed in a batch and the still is operated on a one or two shift basis daily.

The purchase price for new MEK is $2.27 per gallon and the yield for the still is between 13-14 gallons per batch.

The distillation unit paid for itself within 6 months and has been updated to incorporate new Teflon technology outlined earlier.

CONCLUSION:

In order to continue using necessary solvents in their processes, decorators and their suppliers must reprocess them to reduce costs and eliminate wastes. The preferred method from a quality and cost standpoint is indirect heat transfer distillation.

CALPURNIA AND THE STRIP BARN

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How is the Naval Air Rework Facility, Cherry Point, like Caesar's wife Calpurnia? "We must be above reproach!"

Prior to January 1984, the Naval Air Rework Facility, one of North Carolina's largest industrial production facilities, was doing business as usual performing depot level maintenance on a variety of combat aircraft, engines, and components. The normal industrial strength wastes from the operation were being pretreated at our facility's industrial waste treatment plant, then released to flow downstream to our landlord's (Marine Corps Air Station) domestic wastewater treatment plant for final treatment and discharge into the local streams and adjacent shellfish waters. These activities were sanctioned under the National Pollutant Discharge Elimination System (NPDES) permit issued to the Air Station by the Environmental Protection Agency.

In January 1984, a new permit was issued by the State of North Carolina with EPA having an overview responsiblity. North Carolina insisted on tighter discharge parameters and began monitoring daily discharge reports. It was obvious that in order to meet the new discharge requirements, especially with phenol discharge limits of 1 ppm, drastic steps would have to be taken.

Historic industrial wastewater discharge records indicated average daily concentrations of phenols of 55 ppm with a high of 150 ppm. A review of operations immediately pointed a finger at the culprit - the aircraft paint stripping barn - where routinely an aircraft was stripped of all surface coating before being inducted into the overhaul and repair hangar. Stripping a metal clad F-4 class aircraft required three to four 55-gallon drums of strippers containing 20%-25% phenol, or approximately 150 pounds of phenol per drum.

Technology was available to treat and reduce the phenol content of the resulting wastewater to less than 2 ppm, but, one wastewater treatment package offered by a national vendor estimated a cost of ±$10/lb to destroy the phenol, or an overall approximate cost of ±$1500/drum of stripping agent which were purchased for $400/drum. A cost with no return except that we would be allowed to stay in business.

Strippers were available with less phenol content which met specifications. But, we were a victim of the system of having to purchase the cheapest product meeting the specifications. Although there were products available that met the specifications, did the job better, quicker, safer, but cost a little too much.

A four-prong attack was launched simultaneously to eliminate or dramatically reduce phenols in the industrial waste stream.

1. Review and tighten existing specifications covering aircraft paint stripping agents. This was time consuming because of the care taken to ensure that changes would not be allowed that might affect an aircraft surface. With composite structures of aircraft coming into the fleet, this offered a new challenge. The results were good, because some fly-by-night chemical manufacturers that previously met specifications no longer did; consequently, quality products heretofor unobtainable were now available.

2. Search-out-and-test-prove available nonphenolic stripping agents that protect the aircraft and perform efficiently without creating health hazards. Nonphenolic strippers (both acid and nonacid), were tested and proven satisfactory, meeting production requirements of time and cost and reducing the daily range for phenol at the industrial waste treatment plant from a previous high of 150 ppm to a new daily average of less than 2 ppm. Specifications were prepared and Naval Air Rework Facility, Cherry Point moved into a new era of nonphenolic aircraft paint stripping.

3. Develop a program ultimately to eliminate all chemical stripping. Existing technology to replace and/or eliminate the use of chemical stripping for aircraft parts and surfaces did not meet Navy criteria; but several processes were under development. One of the most promising was an old tool with a new twist, plastic media blasting (PMB).

A team of engineers, chemists, and material specialists, was formed to investigate PMB and its potential for use as a tool in our facility. Combining forces with other DoD agencies, we exchanged information drawn from bench-tests on a wide variety of metal and composite surfaces. The team developed a local engineering specification satisfactory to the authority, and on September 18, 1986, the composite underside of an AV8B was stripped of its camouflage with no material damages or structural weakening. The stripping was accomplished in a less than desirable environment with stripper/blaster personnel clad in protective clothing and conditioned-ventilated hoods. Records indicated, and all participants agreed, that even with the primitive work environment, the work was accomplished quicker, at less expense, with no damage to the surfaces, and with less health hazard to the worker.

The overall bottom line indicates that although there will probably always be a need for some chemical stripping, the bulk or 80%-85%, can be eliminated by substituting PMB. The projected labor and material cost savings in the production arenas, coupled with treatment cost reduction, by conservative estimates, can save Naval Air Rework Facility, Cherry Point in excess of one million dollars a year while ensuring NPDES limits will be met.

Engineering is presently underway to retrofit an existing 60ft x 80ft hangar into a blast booth that will accommodate a fighter-class aircraft or helicopters for paint stripping using a four-nozzle blast system with a partial floor media recovery system, properly ventilated to ensure the protection of the workers and the parts being blasted.

4. Review the criteria by which a decision is made to strip an aircraft before overhaul or repair. A technical review board, representing production, quality and reliability assurances, and examination and evaluation departments, inspects each aircraft and determines if the paint system must be stripped prior to refinishing. Every effort is made not to strip except when absolutely necessary, thus reducing solvent waste in a very simple manner, by not using chemical strippers.

The new procedure has eliminated one of every two aircraft which would have routinely been chemically stripped with a phenolic stripper in 1984. The remaining 50% are being scuffed sanded, overpainted, or partially painted.

The program success is attributed to an overall effort on the part of many departments and individuals, including production engineering, materials engineers, chemists, industrial hygienists, and stripper/blasters, with encouragement and strong support of management.

Like Calpurnia, we at Naval Air Rework Facility, Cherry Point, want to be above reproach, whether EPA or the State of North Carolina is or is not looking.

EMISSIONS FROM CHROME PLATING SCRUBBERS AS A FUNCTION OF SCRUBBER LIQUOR CONCENTRATION

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Problem

As additional plating facilities apply scrubbers to their chrome plate ventilation systems, the total chrome emissions to the environment is decreasing. But, our sense of accomplishment is offset by two factors. One, the increased use of atmospheric evaporators for chrome recovery and, two, the heightened awareness that exposure to hexavalent chrome may have significant health effects.

Karen Blanchard and Alfred Vervaert, both of the United States Environmental Protection Agency, spoke at the September AES meeting to demonstrate their concern that chromium emissions may have a negative impact on the public's health. As a result of this concern, there are two points of particular interest to each of us in the plating business. The first and most important is the possibility of adverse health effects that chromium emissions may have on both the general population and ourselves. The second is the probability that our facilities will be required to perform to a Federal or State emissions standard in the near future.

While the United States Environmental Protection Agency is working on the health-related side of this issue, we who are the operators of these systems ought to be working on the technical side. A thorough understanding of the factors related to chromium emissions will give us the best tool to protect both our physical and economic health.

A factor that was addressed in the Environmental Protection Agency's presentation was the use of scrubbers having high concentrations of chrome in the scrubbing liquor which would result in an increased level of emissions. Within our company, we currently have 19 scrubbers on hard chrome plate processes and are installing five more at a new facility in Aguascalientes, Mexico. Historically, these scrubbers were operated at a concentration of 400 PPM and had very low emissions of chrome. Approximately three years ago, we began a program that would increase the concentration of chromic acid in the liquor to 3 ounces/gallon, or approximately a 2% concentration. Because we anticipated that our increased concentration might result in a corresponding increase in total emissions, we initiated a study to quantify this change.

Scrubbers

The scrubbers tested were a conventional design using a packed bed scrubber section and a chevron mist eliminator with two to three inches of drop through the scrubber. The scrubbers were initially designed for a flow rate of 12,000 CFM but have been reduced to 9,000 CFM by eliminating one of the two vaneaxial fans which had been installed in series. This was the result of a lesson learned during a detailed energy study. The vaneaxial fans that were used each had a design pressure rating of 2.3". To achieve the 3.5" to 4" drop that was necessary to move the desired 12,000 CFM, two fans were placed in series by bolting them flange to flange. The result was that the discharge from the first fan generated such a poor inlet condition for the second fan that the second fan could not function properly. Although both fans were pulling near their design HP, we consistently had less than 3" of total drop across the two of them. We have since removed the second fan and are now moving about 9,000 CFM, which has proven to be adequate to control the chromic acid vapors at the plating tank.

Our plating process is the hard chrome plating of piston rings with a relatively thick layer of chrome, thereby requiring several hours of plating time. The gassing, which is a by-product of the plating process, is first suppressed by balls floating on the surface. These balls also serve as an insulator, reducing heat loss from the solution. This insulation is an advantage when we are holding the tank at temperature between loads, but it is a disadvantage when we are applying large amounts of electrical energy to the tank and need to remove the excess heat. The mist that bypasses the balls is collected by a ventilation system which is designed to standards as proposed by the American Conference of Governmental Hygienists and ASHRAE. This mist then passes into the bottom section of the scrubber, up through the packing and through the mist eliminator, and then out through the fan and exhaust stack.

Testing

A method that is commonly used to measure particle emissions from the stack is known as the E.P.A. Method 5 (see Figure #1). The idea is to remove a known and representative quantity of air from the process discharge and capture the specific pollutant that you are interested in. By relating the quantity of the pollutant captured to the quantity of the air removed, we can then calculate both the average concentration and the total emissions.

This concept can also be applied to the measurement of chromic acid. We insert a Pitot and sample combined probe into the stack and remove measured amounts of gas iso-kinetically. This gas then passes through the tubing to a series of impingers. The impingers are filled with a measured amount of distilled or deionized water and are packed in ice. The combination of the condensation and scrubbing action then removes the chromic acid from the exhaust gases and deposits them in the water. Subsequent analysis of the water determines the amount of chromic acid that was collected, which can then be mathematically-related back to the conditions in our stack. A detail that you should always address with this type of a collection system is that the sample equipment must be absolutely clean before you start the test and that the train is carefully rinsed following the test. The chromium in the rinsing water may be a substantial part of the total chrome collected.

Since we had already performed stack testing prior to our 1983 change, we knew that the emissions (with a concentration of 400 PPM of chrome in our scrubbing liquor) were .0075 mg/m^3, or .0067#/day/stack. Our initial assumption was that the chrome in the stack was the result of carryover of the scrubber solution. Based on this assumption, we anticipated that the total chrome emissions would increase linearly with the concentration in the scrubber (see Figure #2). Because of the dramatic increase in concentration which we proposed, we were very concerned about the potentially high chrome emissions and decided to perform a testing program prior to changing the concentration of the scrubber liquor.

The testing program was designed to collect samples with concentrations at the base of 400 PPM and at 1, 2, and 3 ounces/gallon, the 3 ounces/gallon being the highest concentration that we anticipated. When the analytical work was completed and we calculated the final results, we had quite a surprise. The test results showed that the total chromium emissions did not vary linearly with the scrubber liquor concentration and, in fact, were only remotely related. While the concentration in the scrubber increased from 400 PPM to 3 ounces/gallon, or an increase of 55 times, the concentration of chrome in the stack increased from .0073 mg/m^3 to .01273 mg/m^3, an increase of only 1.7 times (see Figure #3) or only 3% of the anticipated increase (see Figure #4). Obviously, nearly all of the .0073 mg/m^3 was from some source other than the carryover of scrubber liquor.

I am convinced that the primary source of chromic acid emissions is acid mist that is being generated at the process tank and passing through the scrubber uncollected. When we look closely, I believe that this hypothesis is supported by information concerning both droplet formation and collection. The droplet formation in the scrubber is the result of two separate actions. The first is the velocity of the air moving across the wetted packing. If you have an average velocity of 600 FPM across the bed area and assuming a peak velocity of twice that or 1,200 FPM in channel within the packing, then the smallest droplet that you would expect is from 2 to 4 microns. The second source of droplet formation is the spray heads but, at 5 PSI or less, the expected droplet size would also be in the same size range, both of which would be easily collected by the chevron type mist eliminator. A chevron section like ours has collection efficiency in excess of 90% at a 5 micron droplet size (see Figure #5).

The rising gas bubbles around the anode and cathodes are generated at very high energies per unit area and tend to be very small. When these bubbles rise to the surface and burst, this minute amount of energy is released. When all of this is combined with the relatively low viscosity of the plating solution at the operating temperature, a very small droplet can be formed. As the acid mist passes through the slots along the edge of the tank, it enters a well proportioned draft housing which has a very low velocity, thus allowing the larger droplets of chromic acid to drop out and be collected by the drainage system in the housing. The remaining carryover is transported to the scrubber by a breach section. The acid mist then enters the packed bed section of the scrubber and is collected primarily by direct impact on the irrigated surfaces. Fortunately, chromic acid is very soluble in water and is therefore easily wetted and captured, thus preventing re-entrainment in the air stream. The liquor, plus its new load of acid, then gravity flows down through the packing and into a holding tank. From this tank, the solution is pumped back to the top of the bed, and the cycle begins again. The scrubbed air then passes out through the mist eliminator and stack.

The maximum of .013 mg/m^3 chromium that is present in our stacks is only a fraction of the 0.10 mg/m^3 concentration that is allowed under the current OSHA rules and is still well below the 0.05 mg/m^3 level that is the current OSHA recommendation. So, theoretically, an employee could work directly in the exhaust stream. The State of Michigan is using an exposure level at the property line of 8.3×10^{-5} ug/m^3, which represents a 10^{-6} risk factor. Obviously, this number can only be determined by modeling and is not practical or even possible to measure. Our opinion is that you might be able to achieve this number in Siberia on a good day.

Irrigated target-type scrubbers operating in the 1" to 10" range have excellent collection efficiencies down to 5 microns and good collection efficiencies down to 1 micron. Consequently, most of the chromic mist bypassing the scrubber is almost certainly below 5 micron and probably below 1 micron. The portion of the emissions that is the result of scrubber liquor carryover will be relatively easy to correct with upgraded mist eliminator sections. Sections that are carefully designed and have the flow through them well distributed can achieve droplet removal to 1 micron.

There is a limit, though, to what can be done with mist eliminators. First, droplets of less than 1 micron just do not have sufficient mass to be removed by a separator that relies upon inertia vs. air friction. Second, at some point, you can have insufficient moisture to irrigate the eliminator surfaces, and salt deposits will quickly develop. This not only degrades the operating efficiency but, in a severe case, can reduce the total air flow through the system. Ultimately, if even lower emissions become necessary, then the only recourse will be to use more sophisticated and energy-intensive scrubbers.

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FIGURE #1

PARTICULATE SAMPLING TRAIN

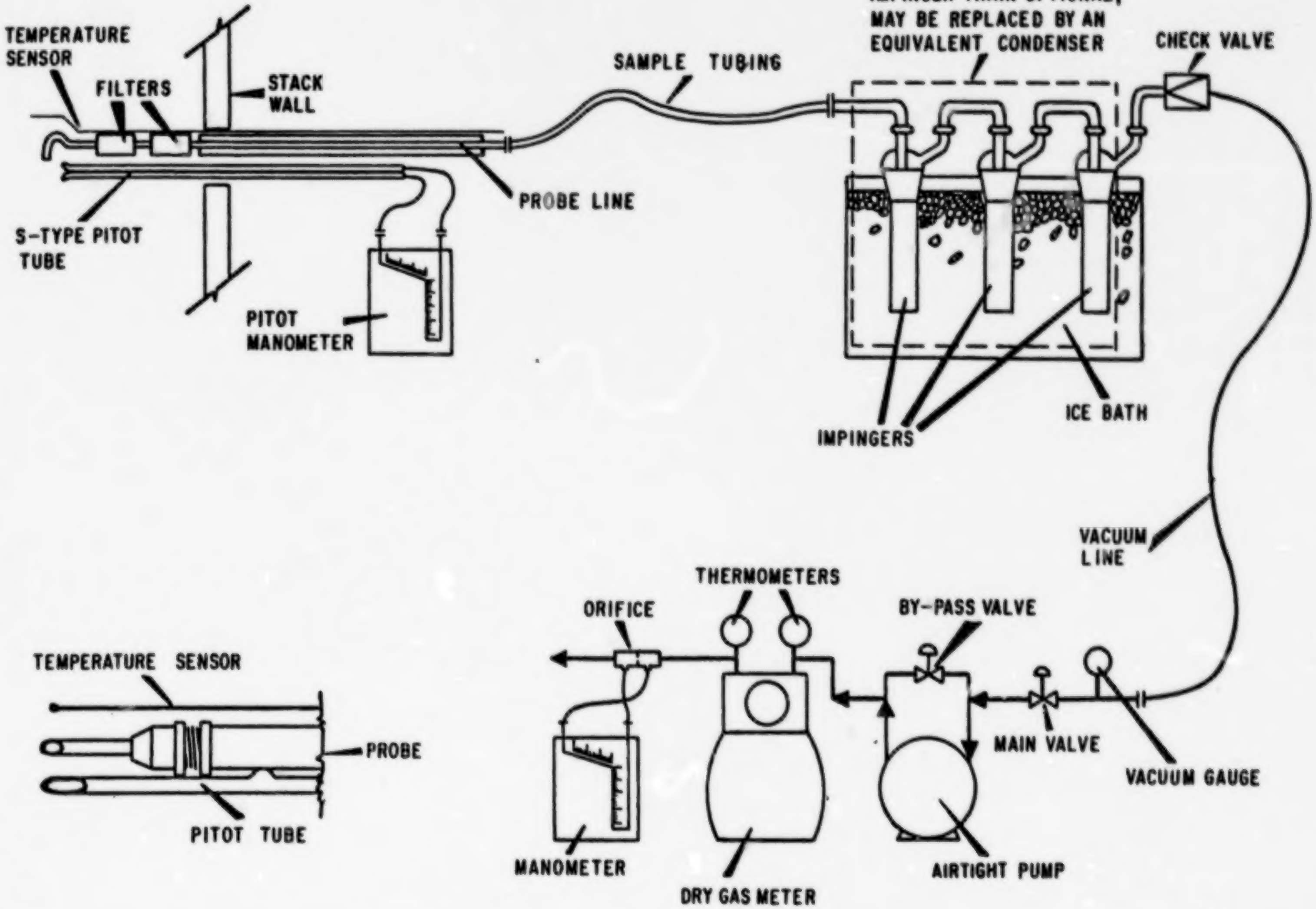

IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSER
TEMPERATURE SENSOR
FILTERS
STACK WALL
SAMPLE TUBING
CHECK VALVE
PROBE LINE
S-TYPE PITOT TUBE
PITOT MANOMETER
IMPINGERS
ICE BATH
VACUUM LINE
THERMOMETERS
ORIFICE
BY-PASS VALVE
MAIN VALVE
VACUUM GAUGE
MANOMETER
DRY GAS METER
AIRTIGHT PUMP
TEMPERATURE SENSOR
PROBE
PITOT TUBE

FIGURE #2

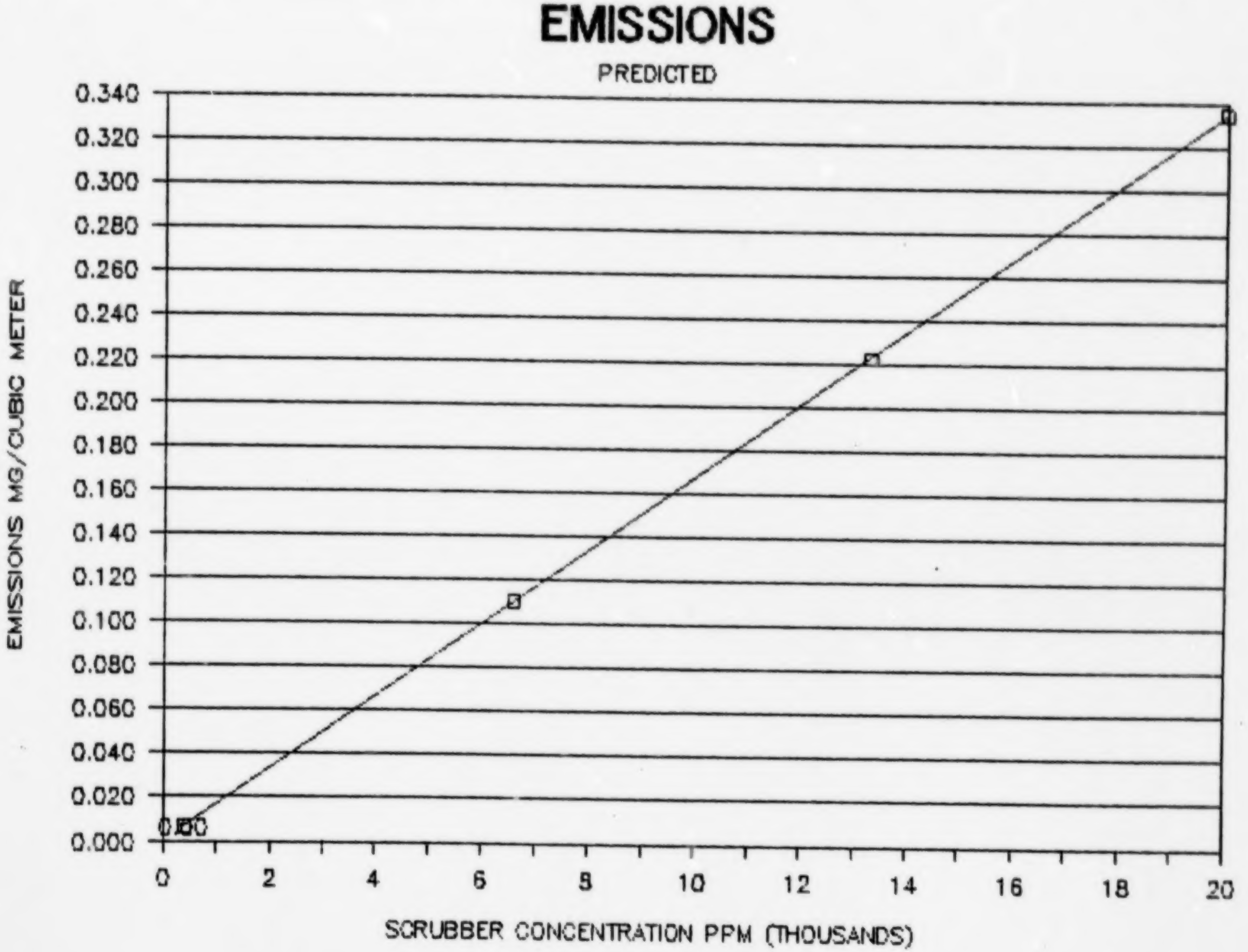

EMISSIONS
PREDICTED
EMISSIONS MG/CUBIC METER
0.340
0.320
0.300
0.280
0.260
0.240
0.220
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
0
2
4
6
8
10
12
14
16
18
20
SCRUBBER CONCENTRATION PPM (THOUSANDS)

FIGURE #3

EMISSIONS

ACTUAL

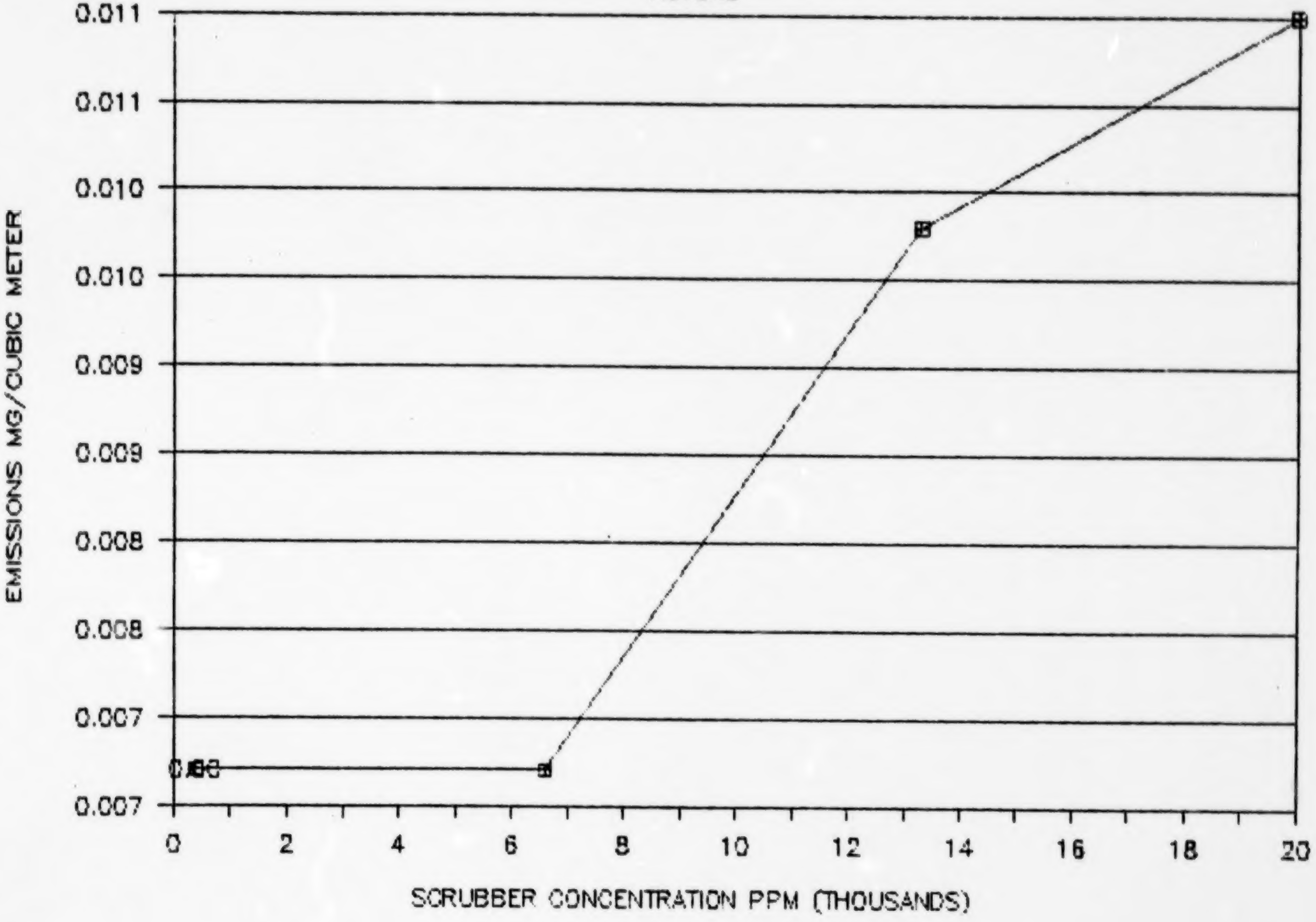


FIGURE #4

EMISSIONS

PREDICTED VS ACTUAL

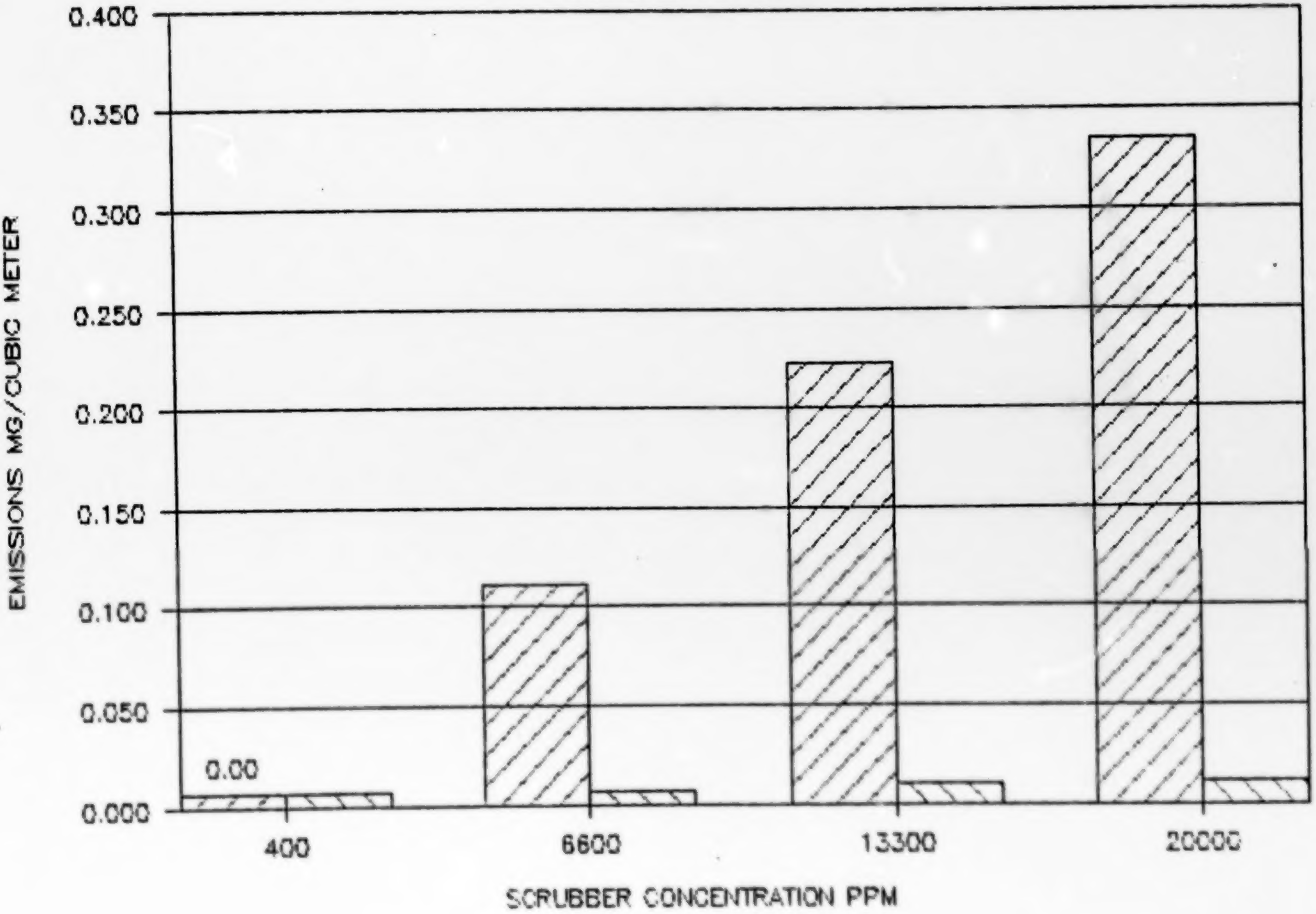
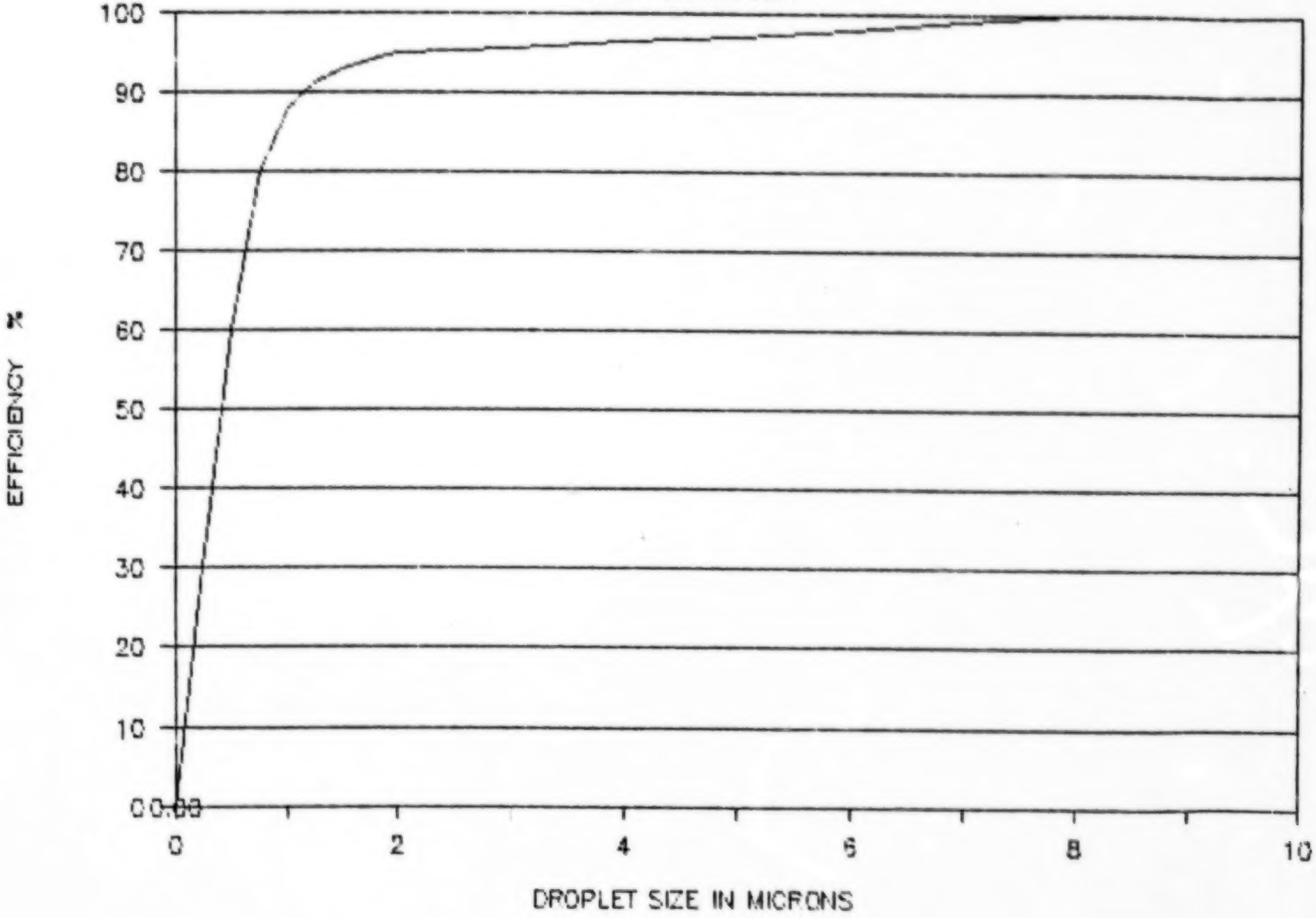


FIGURE #5



EFFICIENCY

MIST ELIMINATOR